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**Synthesis and Properties of Donor/Acceptor Substituted Expanded
Radialenes**

by

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A thesis submitted to the Faculty of Graduate Studies and Research
in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

Department of Chemistry

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Statistics and Properties of Linear Regression Models

Abstract

A linear regression model is considered. The properties of the least squares estimator of the regression coefficients are studied. The distribution of the test statistics for the hypothesis of no linear relationship is also studied.

Keywords

Statistics

Linear Regression

Model

Properties

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Abstract

Cross-conjugated macrocycles are appealing to organic chemists not only because of their aesthetically pleasing structures, but also because the synthetic challenge that they offer is alluring. The Tykwinski group has contributed significantly to the synthesis and study of *iso*-polydiacetylenes (*iso*-PDAs) and expanded radialenes (**[*n*]ERs**), both of which have two-dimensionally (2D) conjugated frameworks. These studies have shown that the *iso*-PDAs and **[*n*]ERs** can be tailored to achieve desirable properties. It has been a longstanding goal in the Tykwinski group to exploit the 2D conjugated framework of the **[*n*]ERs** to gain access to novel push-pull chromophores.

The work described in this Thesis encompasses two central themes: (1) the modular syntheses of donor-acceptor substituted two-dimensionally (2D) conjugated molecules, and (2) the investigation of their structure-property relationships. To this end, a series of *iso*-PDAs and **[4]ERs** were prepared and studied using differential scanning calorimetry, cyclic voltammetry, ¹³C NMR, UV-Vis, and fluorescence spectroscopies.

A one-pot Sonogashira cross-coupling reaction of vinyl triflates and terminal ene-diynes afforded *iso*-PDAs bearing a wide range of functionalites, including trialkylsilyl protecting groups, propargyl alcohols, and electron-donating groups. A complementary approach, which relied on the use of orthogonal alkyne-protecting groups, was developed for the incorporation of electron-withdrawing functionalities. Precursor **[4]ERs**

were synthesized via a generalized protocol involving a sequence of deprotection and Sonogashira cross-coupling reactions between *iso*-PDAs and dibromoolefins. Further functionalization of the **[4]ER** framework with donors/acceptors was achieved via deprotection and subsequent two-fold Sonogashira cross-coupling reactions between the terminal alkynes and various aryl iodides.

The electronic properties of the *iso*-PDAs and **[4]ERs** were contingent upon the nature of the appended groups. However, the electronic properties of the **[4]ERs** did not mirror those of the corresponding *iso*-PDAs. X-Ray crystallography for one **[4]ER** derivative revealed that the radialene framework is not particularly strained, and in the solid state, it maintains a planar structure conducive to effective pi-overlap within the conjugated framework, comparable to other **[4]ERs** known to the Tykwinski group.

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List of symbols

Å angstrom

δ chemical shift

λ_{max} wavelength of maximum absorption

ϵ molar absorptivity

μA microampere

List of abbreviations

A	acceptor
Ac	acetyl
bisDBAs	bis(dehydrobenzoannuleno)benzenes
Bu	butyl
aq	aqueous
ca	approximately
cm	centimeter
CV	cyclic voltammetry
d	doublet
D	donor
decomp	decomposition
DEE	<i>trans</i> -1,2-diethynylethene
DHAs	dehydroannulenes
DSC	differential scanning calorimetry
E_g^{electro}	electrochemical band gap
EI-MS	electron-impact mass spectrometry
ERs	expanded radialenes
ESI	electrospray ionization
Et	ethyl
eV	electron volt
Fc	ferrocenyl
FCC	flash column chromatography

g	gram(s)
GPC	gel permeation chromatography
h	hours
HOMO	highest-occupied molecular orbital
HPEBs	hexakis(phenylethynyl)benzenes
HRMS	high resolution mass spectrometry
Hz	Hertz
<i>i</i>	iso
IR	infrared
LDA	lithium diisopropylamide, LiN(<i>i</i> Pr) ₂
LUMO	lowest-unoccupied molecular orbital
m	multiplet
M	molar
MALDI	matrix assisted laser desorption ionization
Me	methyl (CH ₃)
mg	milligram(s)
MHz	megahertz
mL	milliliter(s)
mmol	millimole(s)
mol	mole(s)
Mp	melting point
MS	mass spectrometry
<i>m/z</i>	mass-to-charge ratio

NLO	nonlinear optical (optics)
nm	nanometer(s)
NMR	nuclear magnetic resonance
ORTEP	Oak Ridge thermal ellipsoid plot
PCC	pyridinium chlorochromate
PDA	polydiacetylene
Ph	phenyl (C ₆ H ₅)
ppm	parts per million
Pr	propyl (C ₃ H ₇)
PTA	polytriacetylene
q	quartet
RAs	radiaannulenes
rt	room temperature
s	singlet
soln	solution
t	triplet
<i>t</i>	tertiary
TBAF	tetrabutylammonium fluoride
TBDMS	t-butyldimethylsilyl
TEE	tetraethynylethene
TES	triethylsilyl
Tf	triflate (SO ₂ CF ₃)
THF	tetrahydrofuran

TIPS	triisopropylsilyl
TLC	thin layer chromatography
	<i>N,N,N',N'</i> -tetramethylethylenediamine
TMEDA	(Me ₂ NCH ₂ CH ₂ NMe ₂)
TMS	trimethylsilyl
TMSA	trimethylsilylacetylene
TPEBs	1,2,4,5-tetrakis(phenylethynyl)benzenes
UV	ultraviolet
UV-Vis	ultraviolet-visible
V	volt
vs	versus

Chapter 1 Introduction: Donor/acceptor substituted two-dimensionally (2D) conjugated chromophores

1.1 Modes of conjugation: linear, cross and omni conjugation

Conjugated organic molecules have been investigated for decades because of their interesting electronic, optical, and nonlinear optical properties.¹ There are three types of conjugation (Figure 1-1) that have dominated these studies: linear, cross and omni conjugation.² The presence of one or a combination of the various conjugation modes plays a key role in the electronic, optical, and nonlinear optical (NLO) properties of the molecules.

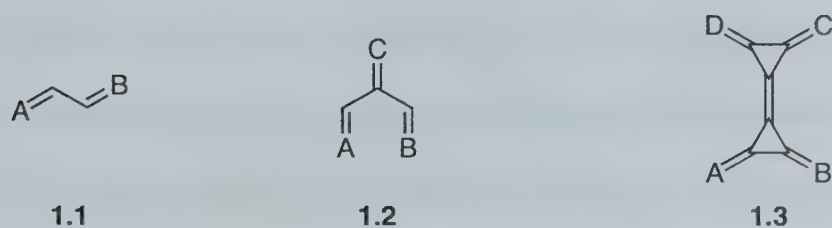


Figure 1-1 Schematic examples of linear, cross and omni conjugation

Linear conjugation is exemplified by a molecule such as **1.1** (Figure 1-1) that possesses a sequence of π -orbitals in a linear array.² Linearly conjugated molecules and oligomers have been extensively studied owing to the plethora of methods and starting materials available for their syntheses.¹ Compound **1.2** is cross-conjugated by virtue of having “three unsaturated groups, two of which although conjugated to a third unsaturated center are not conjugated to each other”.^{3a} Unlike their

linearly-conjugated relatives, cross-conjugated systems have only recently experienced a renaissance, as methods for their syntheses have become more accessible.^{3b} This general interest has been motivated by a desire to gain a better understanding of their unique electronic and optical properties.^{3b-c} Finally, omni conjugation is a property of molecules bearing direct linearly conjugated pathways between all of their appended groups.² While molecules bearing omni conjugation, such as **1.3**, could be interesting toward the development of advanced functional materials,² they will not be covered in this chapter since their properties are not directly relevant to the target molecules of this thesis.

Beyond simply classifying molecules based on the type of π -orbitals, one can also consider the "dimensionality" of a molecule.^{1d,4a} For example, linearly-conjugated molecules are typically one-dimensional (*1D*), which may be schematically defined as the extension of conjugation in a single direction. This is exemplified by molecules such as oligo(phenylenevinylenes) **1.4**, oligo(phenylethynylenes) **1.5**, oligoynes **1.6**, and the oligophenylenes **1.7** (Figure 1-2). The synthesis and study of *1D* conjugated molecules and oligomers have also been extensively reviewed^{1b-d} and will not be discussed further in this chapter.

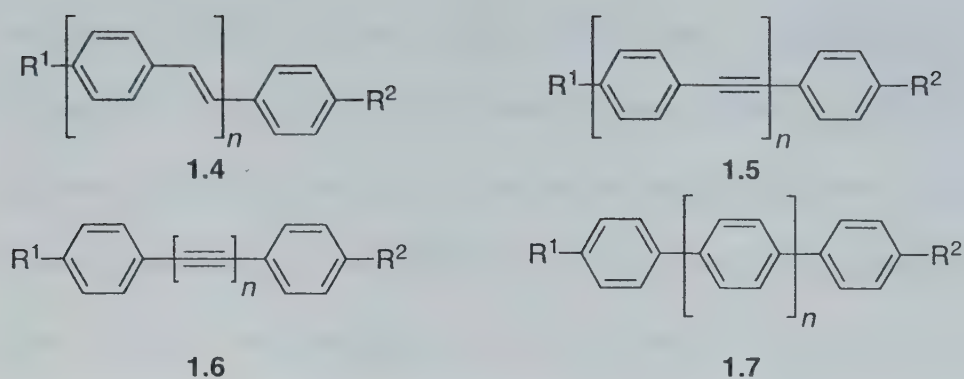


Figure 1-2 Schematic representation of selected *1D*-conjugated systems

The cross-linking of *1D*-conjugated structures can be used to achieve higher spatial dimensionality such as two-dimensionally (*2D*) frameworks.^{4a} Two-dimensional (*2D*) conjugation typically arises when a number of conjugated "arms" radiate from a central conjugated core, and as a result the molecules often possess a combination of linearly and cross-conjugation pathways.⁴ The family of *2D*-conjugated molecules include cruciforms,^{5a} dendrimers,^{5b} and graphitic discs.^{5c} Unlike dendrimers and graphitic discs, cruciforms have dominated the investigation of *2D*-conjugated systems. Cruciforms derive their name from a roughly 'X-shaped' geometry in which the linearly-conjugated segments are approximately orthogonal to each other.^{4a,5} Prominent members of this family of *2D*-conjugated structures (Figure 1-3) include the tetraethynylethenes⁶ (TEEs) **1.8**, tetrakis(phenylethynyl)benzenes⁷ (TPEBs) **1.9**, tetrasterylbenzenes⁸ (TSBs) **1.10**, tetraphenylethenes⁹ (TPEs) **1.11**, the *2D* oligoarylenes¹⁰ **1.12**, and the related hybrids **1.13-1.16**.¹¹⁻¹⁵ Other cruciforms include tetrasubstituted thiophenes,¹⁶

paracyclophanes,¹⁷ spiro compounds,¹⁸ and many others.¹⁹ It is noteworthy that both the 1D- and 2D-conjugated organic frameworks provide a synthetic handle to tune the properties of these molecules and the advancement of the synthesis of both classes of conjugated molecules has come to rely heavily on modern synthetic tools such as metal-mediated cross-coupling reactions.²⁰

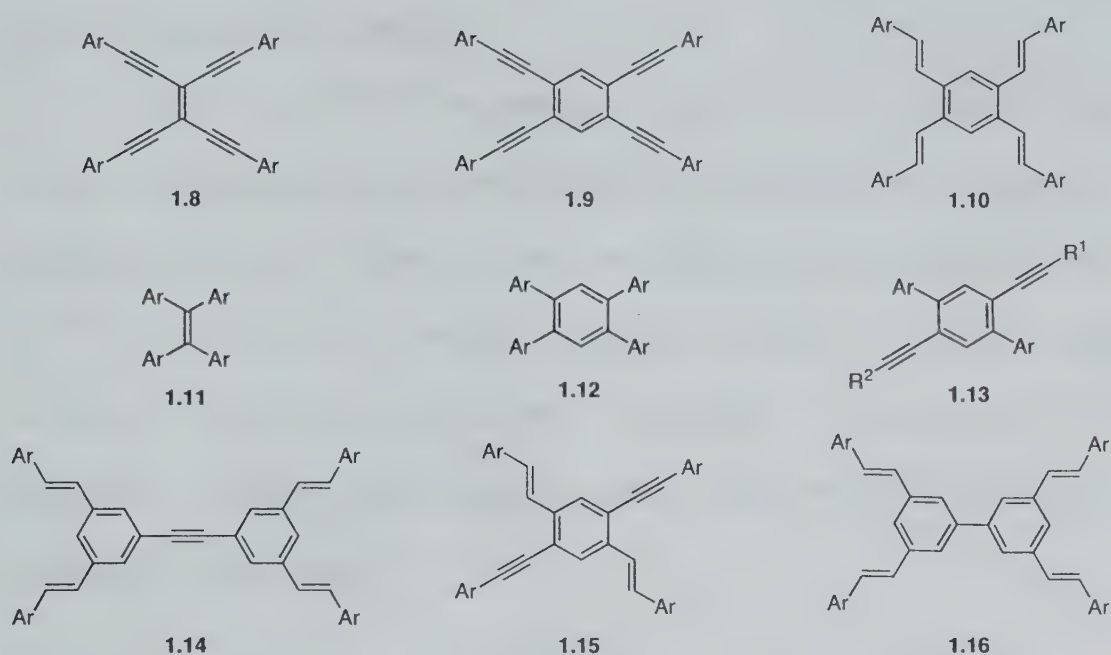


Figure 1-3 Schematic representation of selected examples of cruciforms and related hybrids

One way to tune the optoelectronic properties of these types of molecules is to incorporate strong electron donors (D) and acceptors (A) into 1D- or 2D-conjugated π -framework giving rise to push-pull chromophores (D- π -A).^{1d,21} Push-pull chromophores have been the subject of countless studies because of the potential to be used as materials in molecular electronics.²¹ 1D-conjugated push-pull

chromophores^{1d} have been studied and reviewed extensively and will not be addressed in this chapter. It has been shown that the linking of D and A groups via a 2D-conjugated framework (Figure 1-3) can result in the enhancement of second and third order nonlinear optical responses.^{4a,6b} Of all the cruciforms shown in Figure 1-3, the TEEs **1.8** and TPEBs **1.9** are most commonly used as 2D-platforms for the investigation of structure-property relationships.^{6,7}

The TEE and TPEB frameworks (Figure 1-4) both feature four linearly conjugated pathways (two trans-/para-conjugated **paths a** and two cis-/ortho-conjugated **paths b**) and two cross-/meta-conjugated **paths c**.^{6b,7b} The presence of double bonds in cruciforms **1.10-1.16** and associated bond rotations disrupt the π -conjugation in these types of 2D-conjugated systems. Therefore, examples **10-16** are left out of the discussion in this chapter.

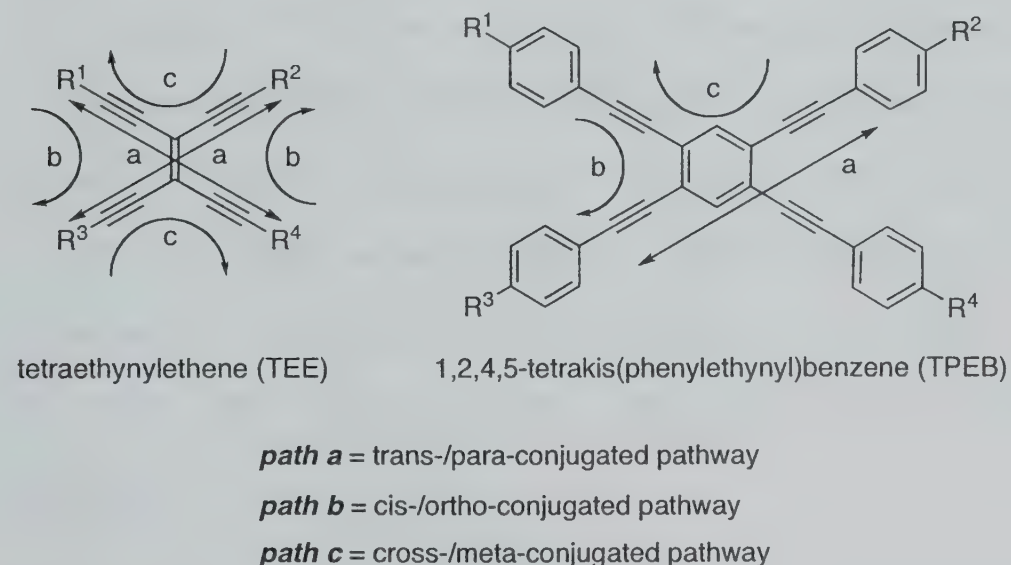


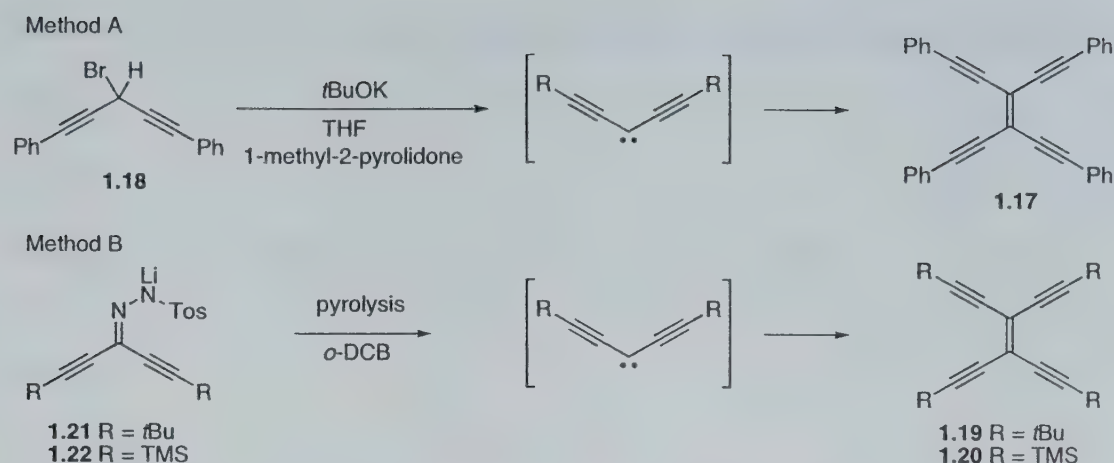
Figure 1-4 Schematic representation of the conjugation pathways of TEEs and TPEBs

This chapter will highlight two central themes of this thesis: The efforts to develop modular approaches toward the synthesis of 2D-conjugated chromophores and the study of their structure-property relationships.

1.2 Strategies for the synthesis of 2D-conjugated molecules

1.2.1 TEEs

The first member of the TEE family **1.17** was reported in 1969 by Hori et al. (Scheme 1-1, Method A).²² Briefly, compound **1.18** was treated with potassium *tert*-butoxide and to yield tetrakis(phenylethynyl)ethane **1.17**. The X-ray crystal structure of **1.17**, provided by Hopf et al. in 1991,²³ showed that the TEE framework allowed coplanar orientation of appended groups and therefore facilitated π -conjugation throughout the system. In the 1970s, Hauptmann²⁴ synthesized the first examples of peralkylated and persilylated TEE derivatives **1.19** and **1.20**, respectively, via pyrolysis of lithium salts of diethynyl ketone tosylhydrazone such as **1.21** and **1.22**, respectively (Scheme 1-1, Method B). Until the early 1990s, the available synthetic tools only allowed access to TEEs bearing four identical substituents and therefore limited the diversity of TEE derivatives needed to further probe structure-property relationships of these interesting molecules.

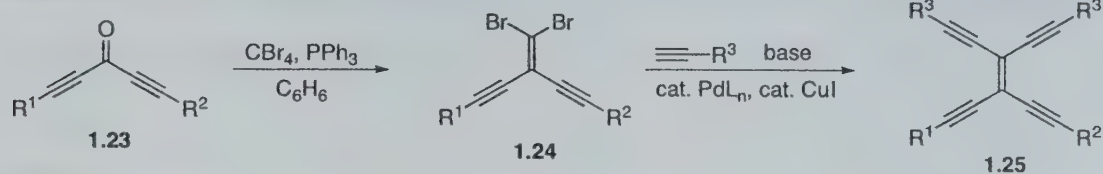


Scheme 1-1 Early work on the synthesis of TEEs

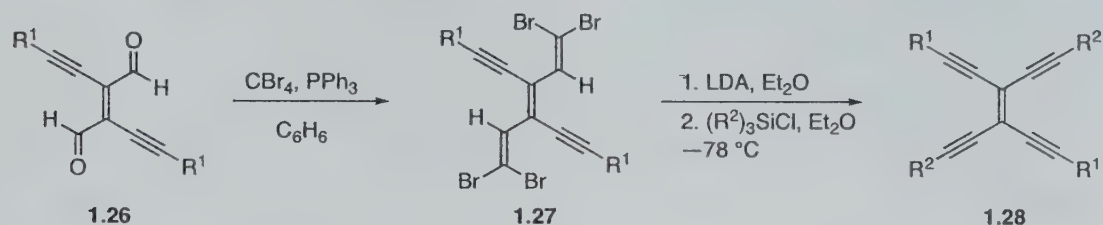
As cross-coupling methodologies found wider applications in the realm of conjugated carbon-rich systems, Diederich and coworkers²⁵ introduced a general protocol, which relied on Pd⁰ catalyzed cross-coupling of 1,1-dibromo-2,2-diethynylethenes with terminal alkynes (Scheme 1-2, Method A). This method was based on the reaction of readily available ketone **1.23** under Ramirez reaction conditions to produce dibromoolefin **1.24** that was then cross-coupled with a terminal alkyne to afford the unsymmetrical TEE **1.25**. A second method²⁶ (Scheme 1-2 Method B) that relied on the use of tetrabromides was devised to gain access to *trans*-substituted TEEs. Thus, dialdehyde **1.26** was subjected to Ramirez conditions to obtain tetrabromide **1.27** which was converted in a two-step synthetic sequence to the desired *trans*-substituted TEE **1.28**. The use of these two methods in concert, with the skillful choice of orthogonal protecting groups, essentially provides any

desired degree and pattern of donor-acceptor substitution about the TEE core.

Method A



Method B



Scheme 1-2 Synthesis of symmetrical and unsymmetrical TEEs

An array of TEE derivatives has been synthesized and studied for their electronic optical and nonlinear optical properties and a representative sample of D/A-substituted TEEs (1.29-1.32) is shown in Figure 1-5.^{6b,27} It has been determined that the 2D-conjugated framework of the TEE is crucial to providing significant third-order NLO properties. Additionally, extension of conjugation and increasing the strength of the donor also enhances third-order NLO response. The donor-acceptor stereochemistry is also recognized as having a small but noticeable effect on the third-order NLO properties. Finally, molecular acentricity is also identified as being essential for significantly enhancing third-order NLO responses. Overall, the structure-property studies of these types of molecules showed that the degree and pattern of D/A-substitution about the TEE core played a key role in the structural, optical as well as the

second and third-order NLO properties.^{7b} Moreover, with the aid of CV and UV-Vis spectroscopy, it has been determined that the TEE core is an electron acceptor; upon introducing strong-electron donors, intramolecular D-A-chromophores are formed.²⁷

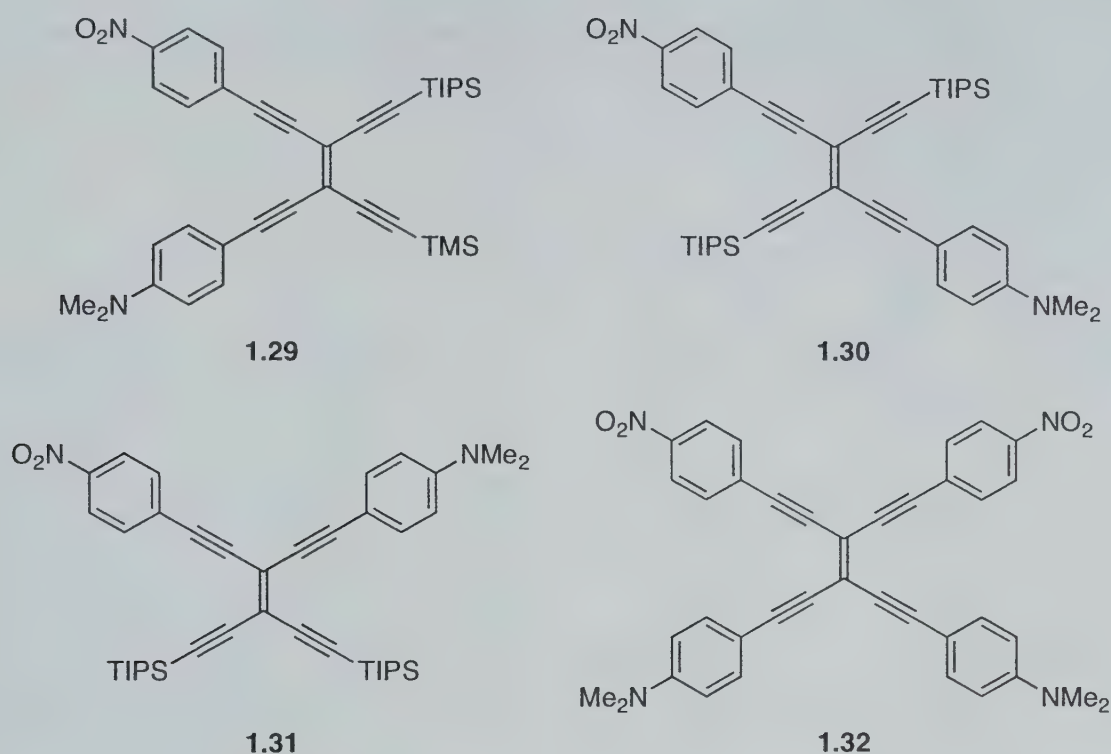


Figure 1-5 Selected D-A substituted TEEs

1.2.2 Dehydroannulenes (DHA), expanded radialenes (ERs) and radiaannulenes (RA)

TEEs are commonly employed as building blocks in the synthesis of highly conjugated carbon-rich macrocycles such as the dehydroannulenes (DHAs),²⁸ expanded radialenes (ERs)²⁹ and radiaannulenes (RAs),³⁰ which are collectively viewed as 2D-conjugated

frameworks (Figure 1-6). The shape-persistent nature of these macrocycles minimizes conformational disorder relative to the acyclic oligomers. More importantly, they provide a synthetic handle to allow the incorporation of donors and/or acceptors and permit the investigation of structure-property relationships in a manner analogous to the TEEs.

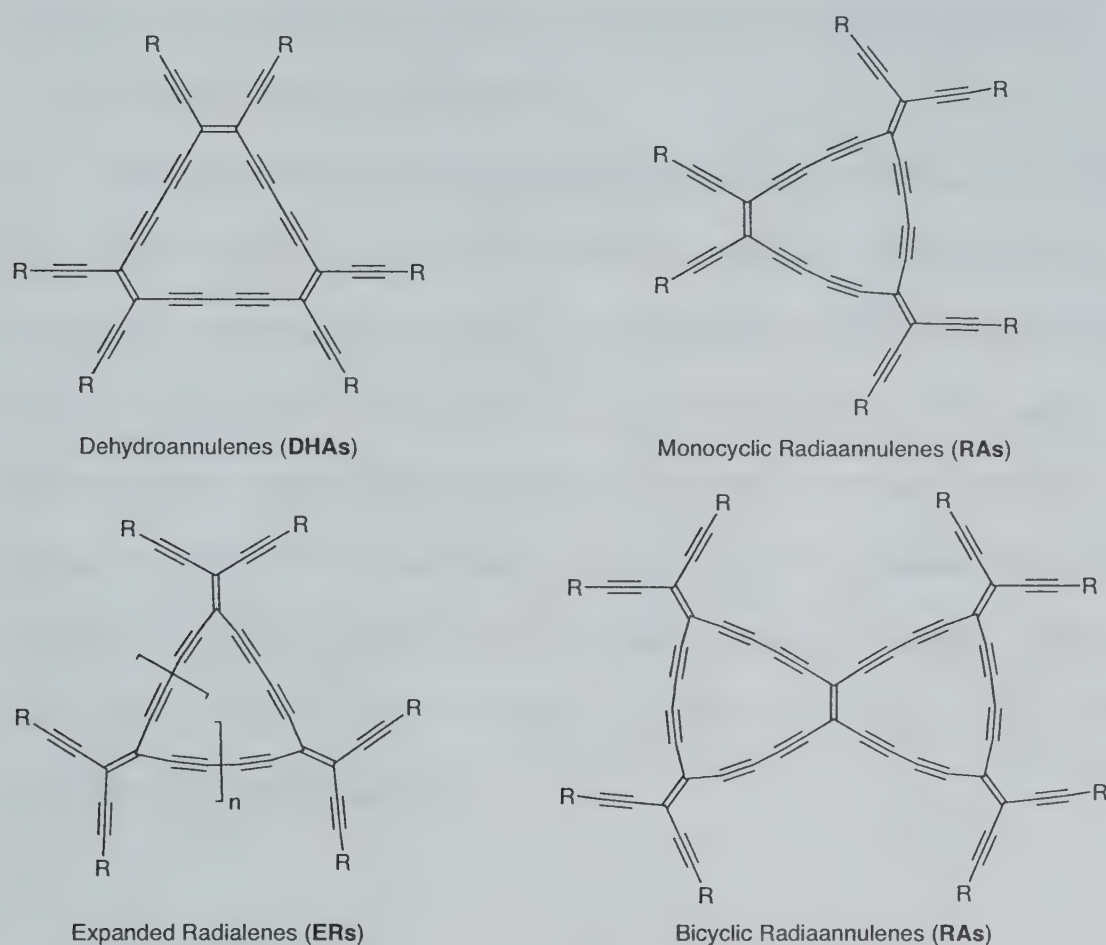
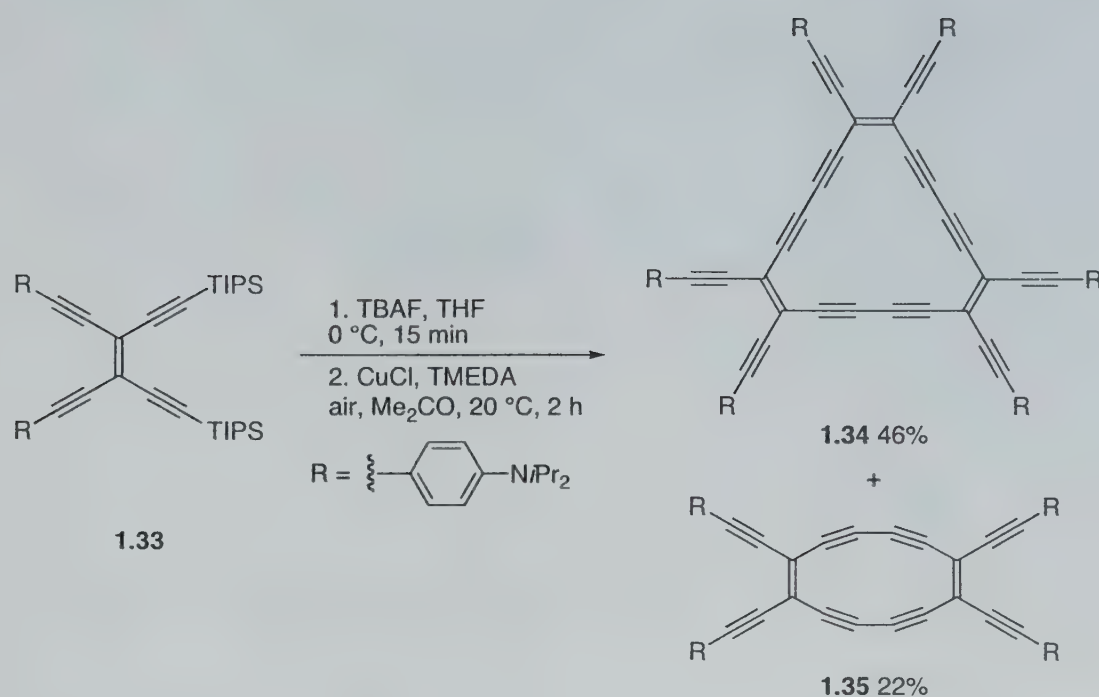


Figure 1-6 Schematic representation of **DHAs**, **ERs**, and **RAs**

The synthetic approach that utilizes TEE building blocks to access **DHAs**, **ERs**, and **RAs** is commonly referred to as acetylenic scaffolding, pioneered by Diederich and coworkers.³¹ The assembly of **DHAs**, **ERs**, and **RAs** takes advantage of the plethora of inter- and intramolecular

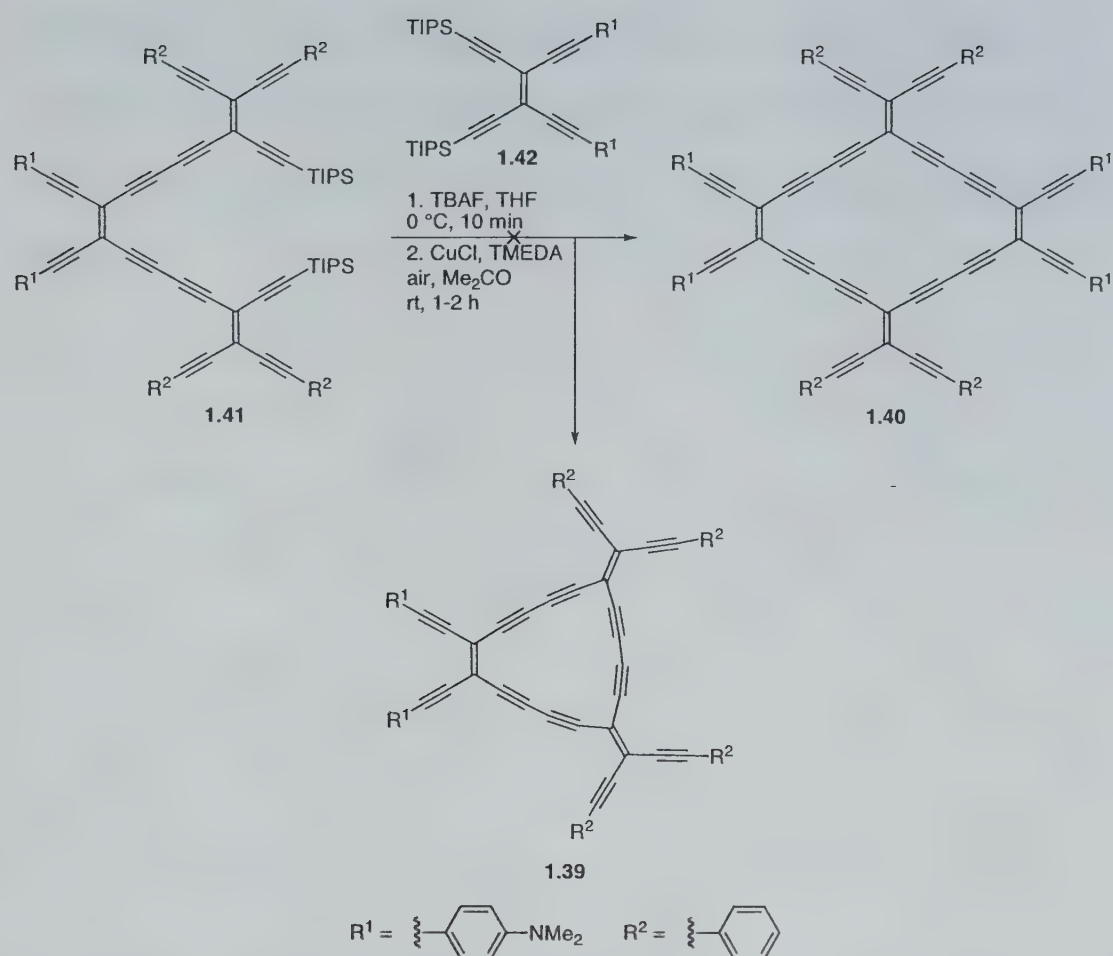
oxidative acetylenic homocoupling methods.³² The main advantage of this approach is that the reaction can often be biased to form the desired oligomeric macrocycle. The disadvantage lies in the formation of larger acyclic and cyclic oligomers that tend to plague the purification step. The slow addition of one of the terminal alkynes to the reaction mixture can, however, be employed to prevent the formation of undesired oligomers, i.e. pseudo-high dilution conditions.³²

Diederich and coworkers reported the synthesis of **DHAs 1.34** and **1.35** in 2006 (Scheme 1-3).²⁸ TEE **1.33** was desilylated and immediately subjected to Hay reaction conditions to provide **DHAs 1.34** and **1.35** in 46 and 22% yield, respectively, after column chromatography. The authors noted that the yield of **DHAs 1.34** and **1.35** was significantly improved compared to the *N,N*-dimethylanilino analog, and this achievement was attributed to the presence of the *N,N*-diisopropylanilino moieties. **DHAs** containing strongly electron-donating and withdrawing groups via this method are yet to be realized.



Scheme 1-3 Synthesis of **DHAs 1.34 and 1.35**

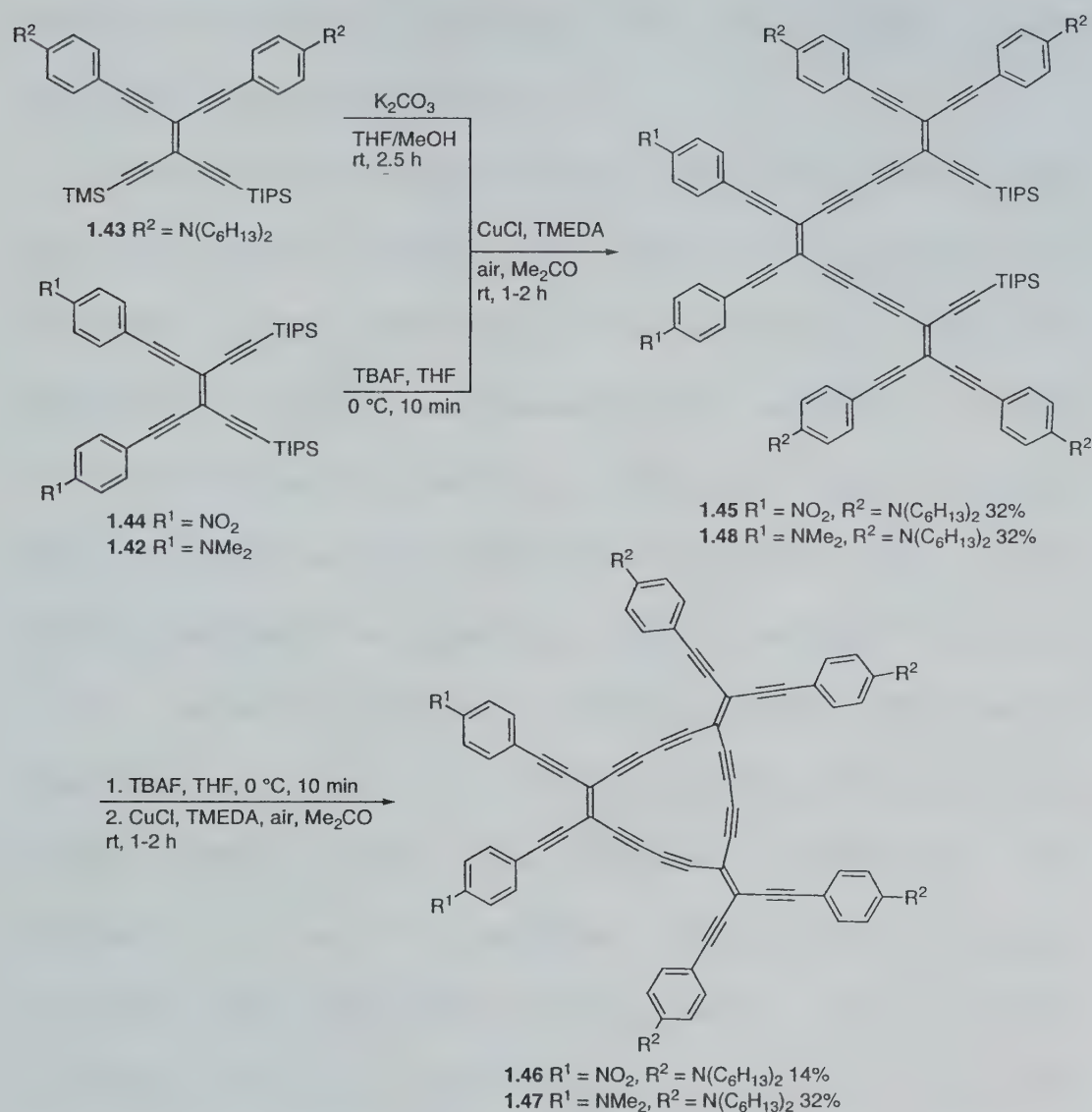
Diederich and co-workers reported a concise synthesis of the first member of the family of **ERs** containing a butadiynyl unit as the π -spacer.²⁹ A representative synthesis of **ERs** is exemplified in Scheme 1-4. TEE **1.36** was desilylated with TBAF and, under Hay conditions, was oxidatively homocoupled to provide **[3]ER 1.37** and **[4]ER 1.38** 8 and 10% yield, respectively. To date this approach has had limited success in producing **ERs** that feature strongly electron-withdrawing and donating groups.



Scheme 1-5 Attempted synthesis of **1.40** and serendipitous formation of **1.39**

The intermolecular oxidative acetylenic homocoupling approach to the assembly of **RA**s has had modest success in producing D-A substituted monocyclic **RA**s³⁰ and is described in Scheme 1-6. Briefly, the TMS group of *gem*-TEE **1.43** was selectively removed using K₂CO₃ and then combined with a solution of the *in situ* bisdeprotected **1.44** under Hay coupling conditions to provide the trimeric TEE **1.45** in 32% yield. Compound **1.45** underwent global desilylation using TBAF followed by intermolecular macrocyclization under Hay coupling conditions to yield the monocyclic radiacene **1.46** in 14% yield after column

chromatography. The donor-substituted **RA 1.47** was prepared in a slightly improved yield of 32% from the trimeric TEE **1.48**, which was derived from monomeric TEEs **1.42** and **1.43** in a manner analogous to **RA 1.46**.



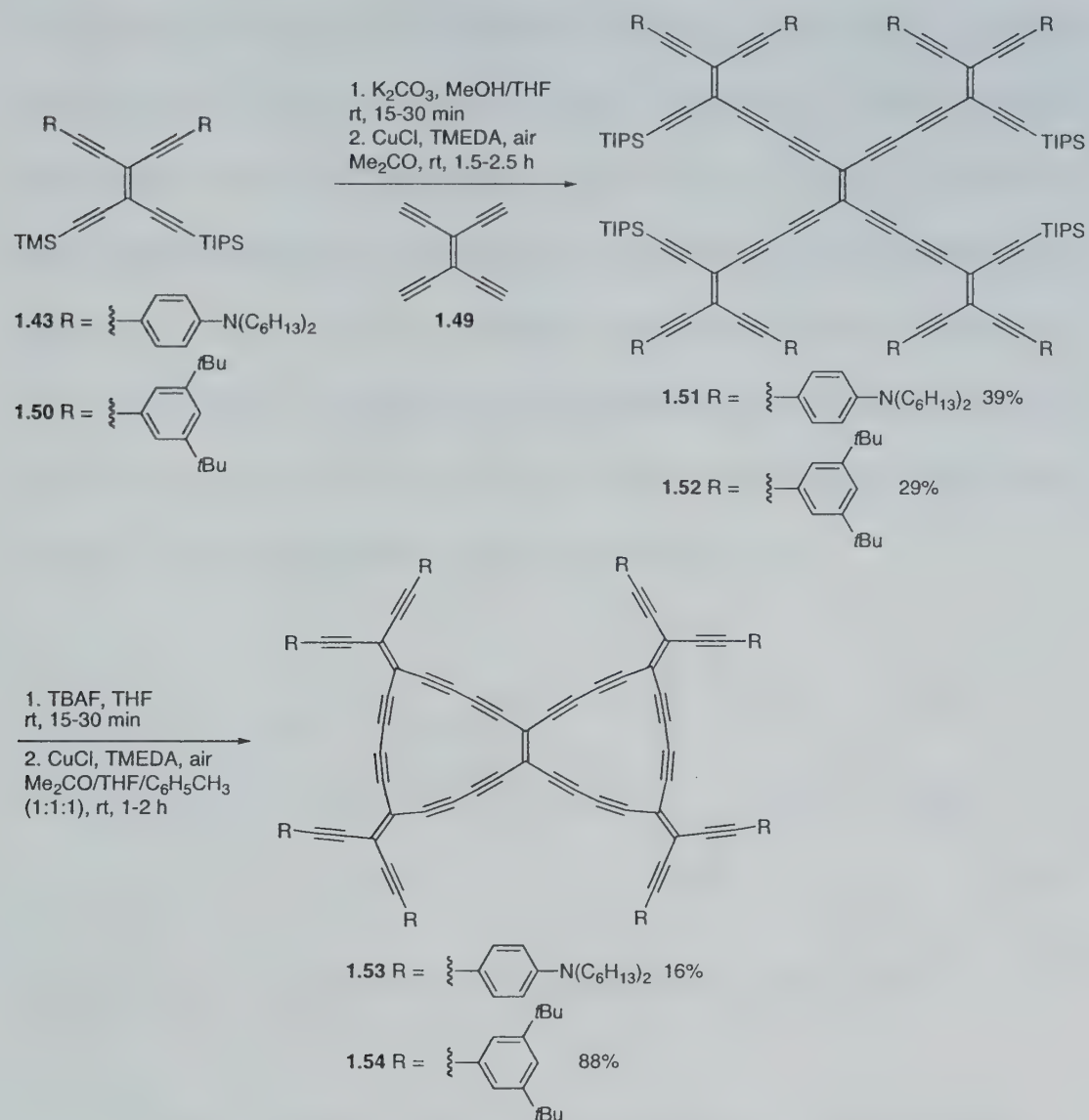
Scheme 1-6 Representative synthesis of **RAs 1.46** and **1.47**

Bicyclic perethynylated **RAs** have also been synthesized by the Diederich group using TEE acetylenic scaffolding.³⁰ The synthesis of two

RAs is described in Scheme 1-7. The parent TEE **1.49** was reacted with monodeprotected TEEs **1.43** and **1.50** to yield pentameric TEEs **1.51** and **1.52** in 39 and 29% yield, respectively, after gel-permeation chromatography (GPC). Global desilylation of pentamers **1.51** and **1.52** followed by ring closure via slightly modified Hay coupling conditions provided the bicyclic **RA**s **1.53** and **1.54**.

It has been shown electrochemically that the **DHAs**, **ERs**, and **RA**s are potent electron acceptors, and, upon the introduction of *N,N*-dialkylanilino groups, intramolecular D- π -A chromophores with unique optoelectronic properties are formed.^{21,30} For example, it has been determined that the first reduction potential of the bicyclic radiaanolene **1.54** (−0.83 V) is lower than that of buckminsterfullerene (C₆₀, −1.02 V), which is proclaimed to be a good organic electron acceptor. The presence of the peripheral dialkylanilino groups not only enhances the optoelectronic properties, but also increases solubility and stability of the electron accepting all-carbon cores. Furthermore, the introduction of two nitrophenyl groups as in D-A substituted monocyclic **RA** **1.46** does not significantly affect the electron-accepting abilities relative to donor-substituted analogs, e.g. **1.47**.³⁰ Finally, a comparison of the UV-Vis spectra of **DHAs**, **ERs** and **RA**s containing the same number of peripheral anilino groups, reveals that the propensity of the macrocycles to participate in intramolecular D-A interactions depends largely on the arrangement of

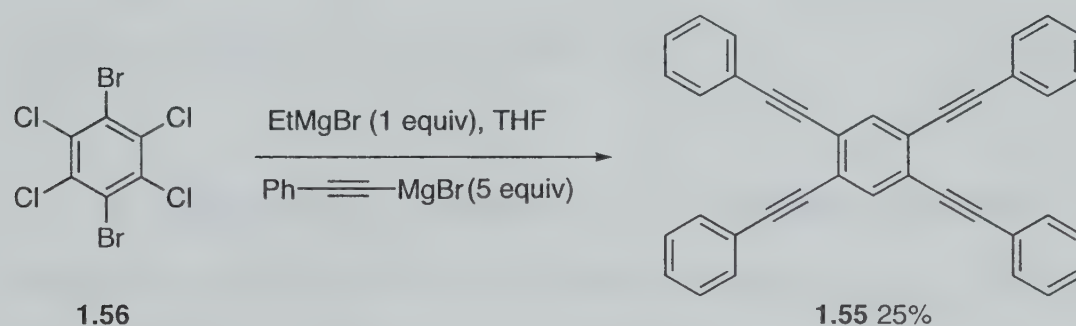
the TEE units in the framework. The authors noted that theoretical studies are still needed to confirm this observation.³⁰



Scheme 1-7 Synthesis of bicyclic RAs **1.53** and **1.54**

1.2.3 Tetrakis(phenylethynyl)benzenes (TPEBs)

TPEBs have been identified and exploited by Haley and coworkers as suitable 2D-conjugated frameworks for the preparation of push-pull chromophores.⁷ Similarly to the TEE framework, TPEB facilitates coplanarity among the appended groups and, therefore, allows the systematic investigation of the effect of structure-property effects based on degree and pattern of D/A substitution. One of the earliest syntheses of the parent TPEB, tetrakis(phenylethynyl)benzene **1.55**, was performed by Hart and coworkers³³ in 1987 using **1.56**, phenylethynyl magnesium bromide, and ethymagnesium bromide (Scheme 1-8).

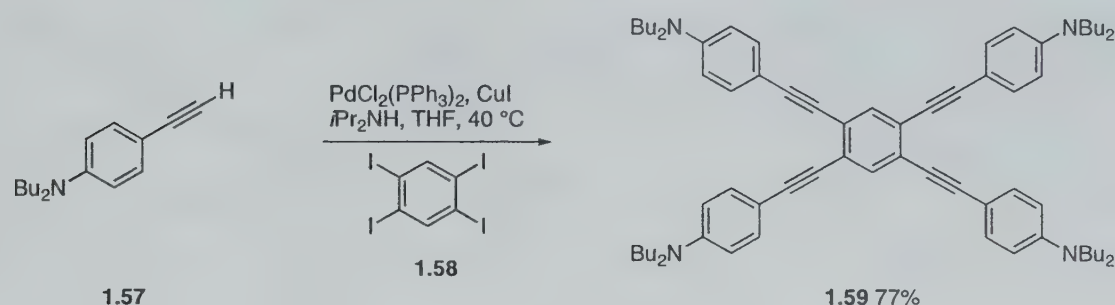


Scheme 1-8 Early synthesis of tetrakis(phenylethynyl)benzene **1.55**

As seen with the TEEs, the metal-mediated cross-coupling has played a key role in the advancement of the synthesis and study of TPEBs. Haley and co-workers⁷ introduced the rational synthesis of a rich variety of TPEBs and have investigated their structure-property relationships. The synthetic strategy relied heavily on the Sonogashira cross-coupling reaction³⁴ to assemble and decorate the TPEB framework. Moreover, the preferential reactivity of aryl iodides in the presence of aryl

bromides was exploited to incorporate donors and acceptors in the desired positions.⁷

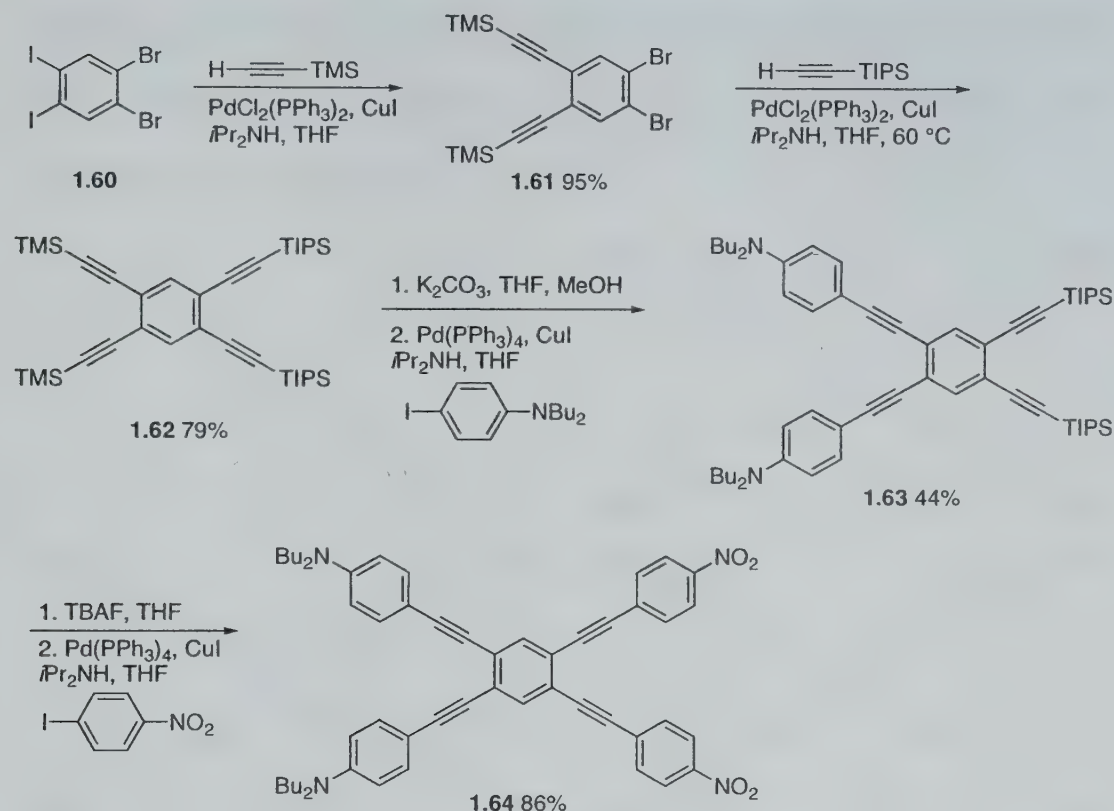
The synthesis of a TPEB containing identical substituents is straightforward as described in Scheme 1-9. The readily available precursor **1.57** underwent a four-fold Sonogashira cross-coupling reaction with 1,2,4,5-tetraiodobenzene **1.58** to yield TPEB **1.59** in 77% yield.^{7a}



Scheme 1-9 Synthesis of tetradonor TPEB **1.59**

A representative synthesis of a D-A functionalized TPEB^{7b} is described in Scheme 1-10. 1,2-Dibromo-4,5-diiodobenzene **1.60** was reacted with TMS-acetylene in a two-fold Sonogashira cross-coupling reaction to provide compound **1.61** in 95% yield. Compound **1.61** then underwent a second two-fold Sonogashira cross-coupling reaction with TIPS-acetylene to provide orthogonally-protected TPEB **1.62**. The TMS groups in **1.62** were selectively removed using K_2CO_3 , and the resulting terminal diyne was reacted with *N,N*-dibutyl-4-iodoaniline to afford **1.63** in a modest yield of 44%. Removal of the TIPS groups followed by Sonogashira cross-coupling with 4-iodo-nitrobenzene afforded D-A substituted TPEB **1.64** in very good yield. It is noteworthy that this method

was later used to synthesize D-A TPEBs containing weakly^{7e} and inductively^{7g} electron-withdrawing groups, thus demonstrating the broad scope of this approach.



Scheme 1-10 Representative synthesis of TPEB **1.64**

Structure-property relationships for TPEBs (Figure 1-7) have been investigated including the effects of donor and/or acceptor substitution, symmetry, and conjugation paths. Several salient points are provided here.^{7b} It has been shown that λ_{max} is significantly red-shifted on going from parent TPEB **1.55** to donor-substituted **1.64**. In terms of donor-acceptor stereochemistry, (**1.64-1.66**), it has been shown that larger net dipoles and linearly conjugated pathways resulted in the greatest

bathochromic shifts in the UV-Vis spectra. Fluorescence spectroscopy reveals that the best quantum efficiencies were obtained for donor-substituted TPEBs.^{7b,7f} It is noteworthy that **1.59** and **1.66** have been investigated for their two-photon absorption³⁵ properties showing that donor-substitution increases two-photon absorption more strongly than does acceptor-substitution.^{7c}

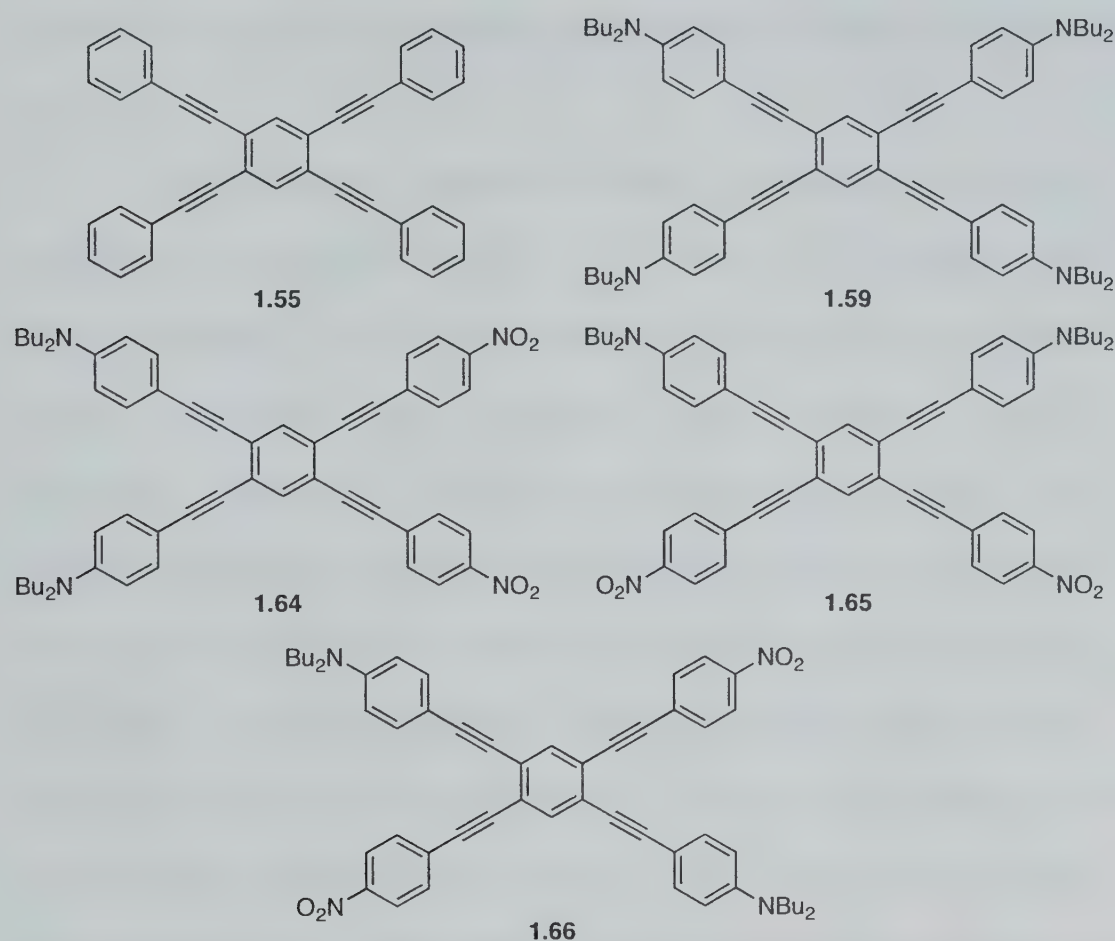


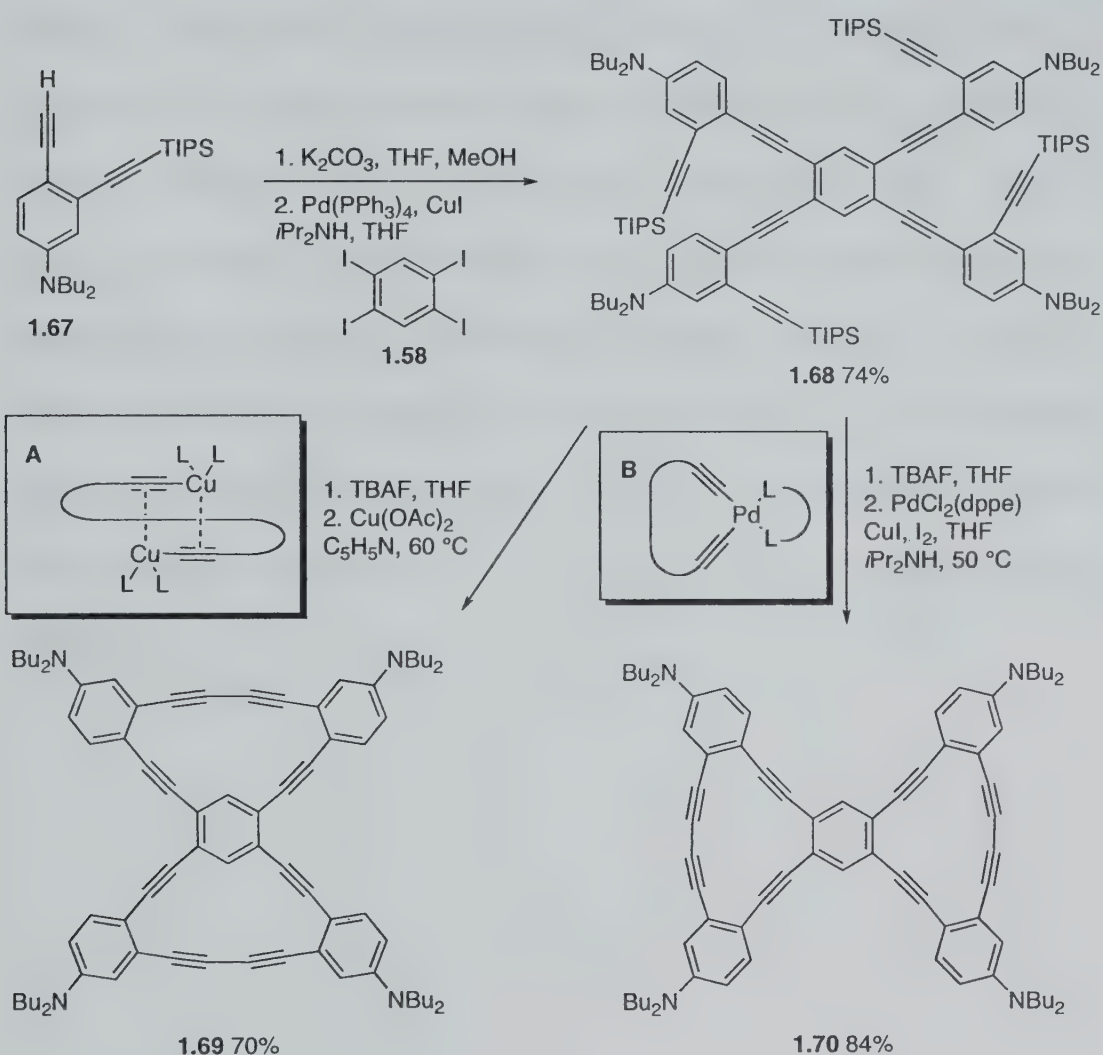
Figure 1-7 TPEBs studied for structure-property relationships

The use of the TPEB framework in phenylacetylene scaffolding³⁶ toward the synthesis of donor-acceptor substituted bisannulenes was reported by Haley and coworkers.^{7b} Overall, it was envisioned that DBAs

would have enhanced linear and nonlinear optical responses, as a result of being constrained into a cyclic arrangement. The incorporation of donors and acceptors, using a similar approach as developed for the TPEBs, would allow the effects of substitution pattern on the electronic and optical properties to be investigated. A comparison of similar substitution patterns in TPEBs and DBAs should give further insight into the role of planarity in mediating communication between donors and acceptors.

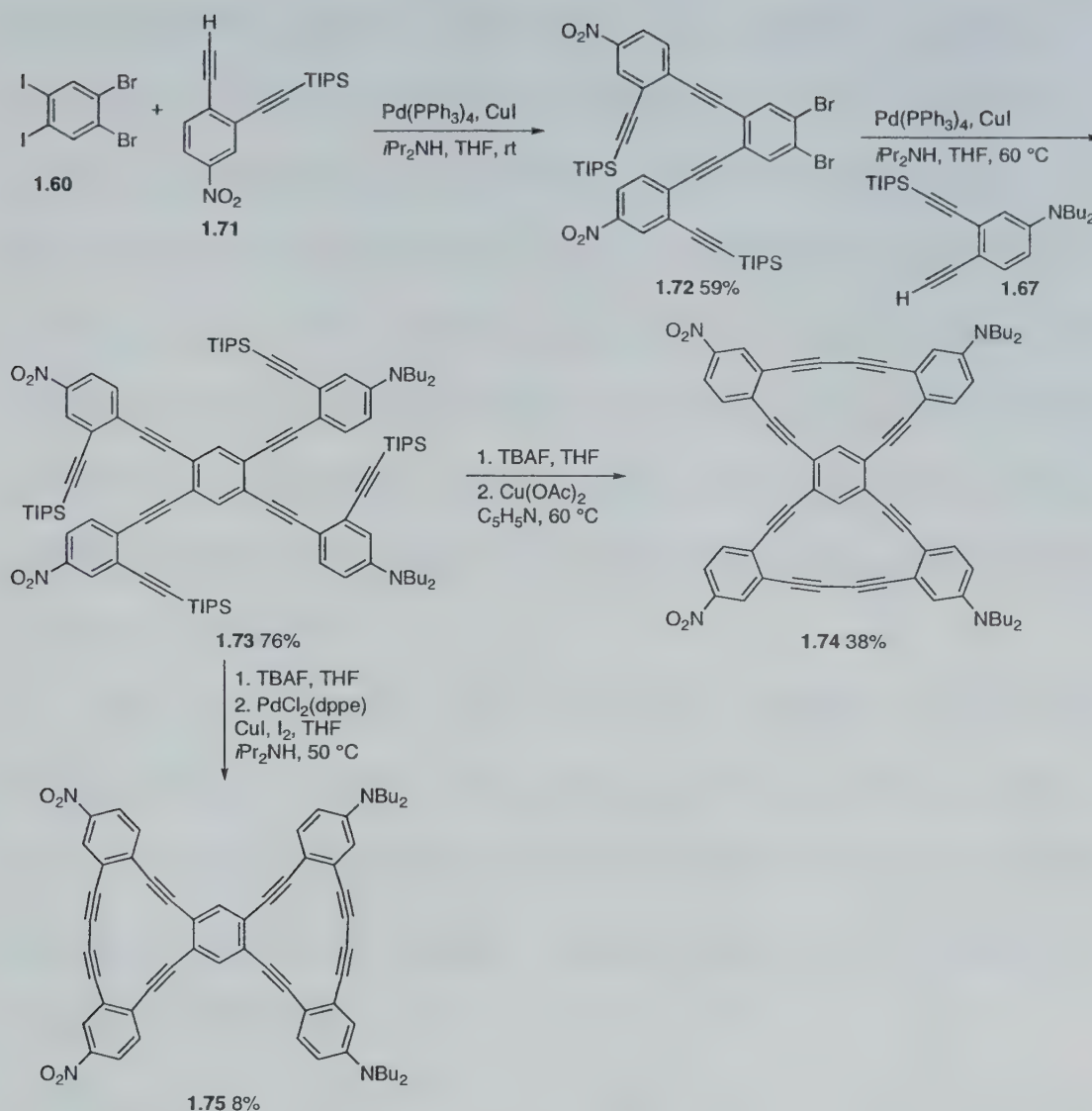
A representative synthesis of DBAs containing four identical substituents is shown in Scheme 1-11.^{7b} A four-fold Sonogashira cross-coupling between 1,2,4,5-tetraiodobenzene **1.58** and **1.67** afforded the common precursor **1.68**. Compound **1.68** underwent exhaustive desilylation, followed by intramolecular homocoupling under Glaser-Eglinton conditions, to provide bis[15]annulene **1.69** in moderate yield. The authors attributed the preferential formation of the bis[15]annulene **1.69** to the Cu-acetylide adopting a pseudo-*trans*-configuration (Figure 1-11, inset A) before reductive elimination.^{7b} Conversely, desilylation of **1.68** followed by Pd-catalyzed oxidative homocoupling resulted in the formation of the bis[14]annulene **1.70** in 84% yield. The preferential formation of the bis[14]annulene **1.70** was attributed to the presence of the bidentate diphenylphosphinoethane (dppe) ligand which forces the Pd-acetylide intermediate (Figure 1-11, inset B) adopt a *cis*-configuration before the reductive elimination step.^{7b} Moreover, the authors stated that a careful

choice of ligands could be used to improve the performance of this reaction. For example, it was found that by using dppe, the bis[14]annulene was formed exclusively, while PPh_3 ligands resulted in the formation of a 4:1 mixture of the DBAs with a strong preference for the bis[15]annulene. This observation was attributed to the PPh_3 ligand favoring *trans*-addition and the *cis*-bidentate dppe ligand favoring *cis*-addition of the acetylides prior to reductive elimination.^{7b}



Scheme 1-11 Synthesis of tetradonor DBAs **1.69** and **1.70**

D-A substituted bis[14]- and bis[15]annulenes bearing different substitution patterns were synthesized by taking advantage of the greater reactivity of iodides over bromides in the sp^2 - sp cross-coupling.^{7b,7g} A representative synthesis is shown in Scheme 1-12. Briefly, 1,2-dibromo-4,5-diiodobenzene **1.60** was reacted with **1.71** via a Sonogashira cross-coupling to provide compound **1.72**. Compound **1.72** underwent a second two-fold Sonogashira cross-coupling with **1.67** to provide the key precursor **1.73** in very good yield. Global desilylation of **1.73** followed by oxidative intramolecular macrocyclization conditions under Eglinton conditions provided bis[15]annulene **1.74** in 38% yield, while Pd-catalyzed homocoupling conditions afforded bis[14]annulene **1.75** in 8% yield. The authors noted that all efforts to improve the yields of D-A substituted bis[15]- and bis[14]annulenes were thwarted by intermolecular oxidative homocoupling reactions that form large quantities of oligomeric by-products.^{7b}

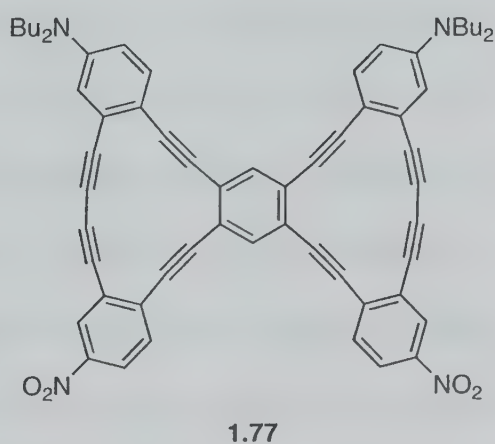
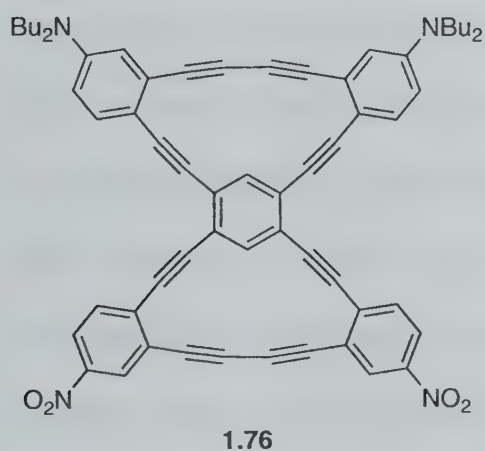


Scheme 1-12 Synthesis of D-A **1.74** and **1.75**

Structure-property relationships of DBAs **1.69-1.70**, **1.74-1.77** have been investigated using UV-Vis and fluorescence spectroscopies.^{7b} As predicted, UV-Vis spectroscopy shows an increase in overall conjugation effectiveness on going from non-planar TPEBs to the planar DBAs. UV-Vis spectroscopy shows that the longest-wavelength λ_{max} of the DBAs is significantly bathochromically-shifted relative to the TPEBs bearing the

same substitution pattern. Furthermore, D-A substitution results in a lowering of the HOMO-LUMO gap relative to donor-substitution as evidenced by the significant bathochromic shifts of the lowest energy λ_{max} and the development of strong charge transfer bands in the UV-Vis spectra. In terms of the orientation of donors and acceptors, larger net dipoles and linearly conjugated pathways give the greatest bathochromic shifts. Fluorescence spectroscopy has shown that the tetra-donor DBAs **1.69** and **1.70** afford the best quantum efficiencies, an observation already seen for the TPEBs.^{7b,7f}

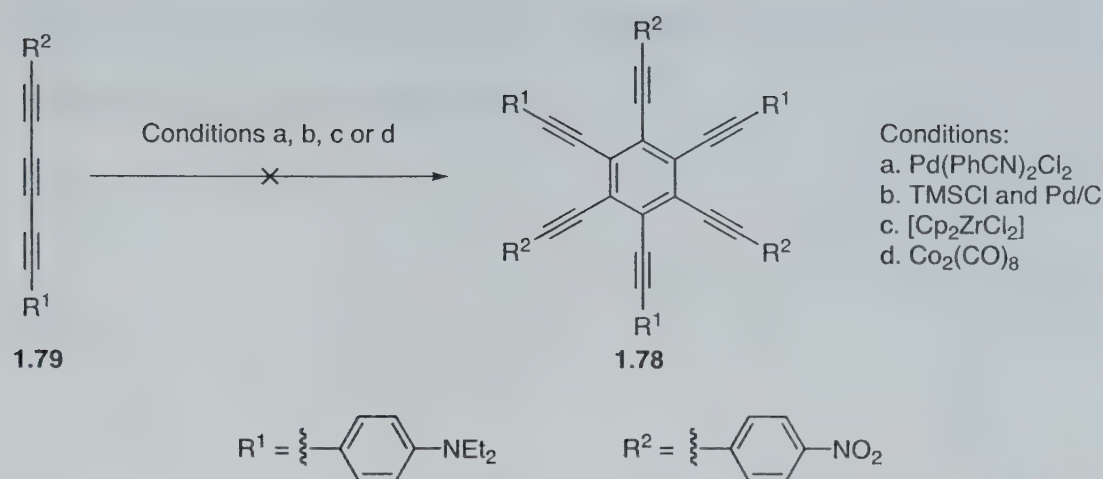
The authors also report that D-A substituted bis[15]- and bis[14]annulenes **1.74-1.77** exhibit self-association properties in solution that give dimers via face-to-face π - π stacking.^{7b} Bis[15]annulenes **1.74** and **1.76** have a greater propensity to aggregate than their bis[14]annulene analogs **1.75** and **1.77**.



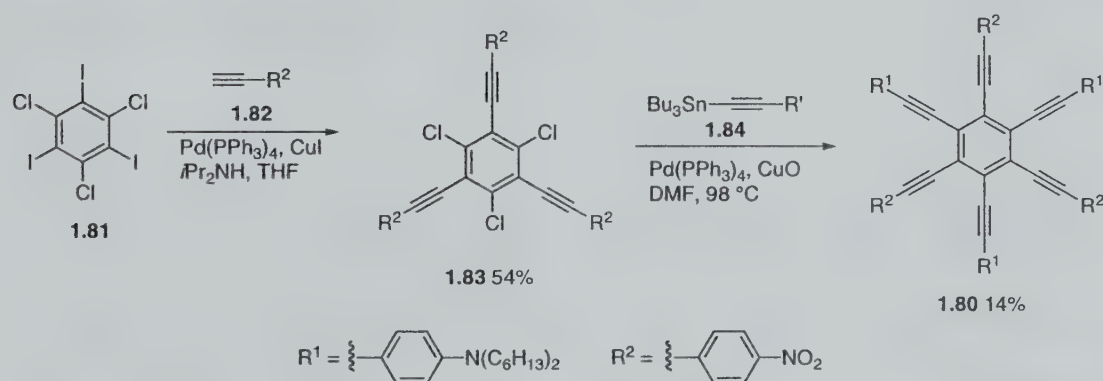
1.2.4 Hexaphenylethynylbenzenes and phenylacetylene macrocycles

Another class of 2D-conjugated platforms used for the preparation of push pull chromophores is known as the hexaphenylethynylbenzene (HPEBs).³⁷ The HPEB building block has been used successfully to produce materials with interesting electron-transfer^{37c} and liquid crystalline properties.^{37d,e} The incorporation of alternating electron-donors and electron-acceptors onto the HPEB core gives rise to hexasubstituted push-pull chromophores with the potential to be used for applications in nonlinear optics.^{37f}

Gleiter and coworkers reported the first synthesis of functionalized HPEBs such as **1.78** in 2004.^{37f} It is noteworthy that functionalized HPEBs were unknown prior to the synthesis of **1.78**. The initial synthetic efforts toward **1.78** were made using a metal-mediated cyclotrimerization reaction of **1.79** using several different catalysts (Scheme 1-13). However, this approach was unsuccessful in producing **1.78**. A stepwise approach was used to synthesize **1.80** (Scheme 1-14) that took advantage of the preferential reactivity of aryl iodides in the presence of aryl chlorides for the placement of donors and acceptors. Compound **1.81** underwent a three-fold Sonogashira cross-coupling with 4-ethynynitrobenzene **1.82** to produce compound **1.83** in 54% yield. Stille cross-coupling of **1.83** with **1.84** provided the desired HPEB **1.80**.



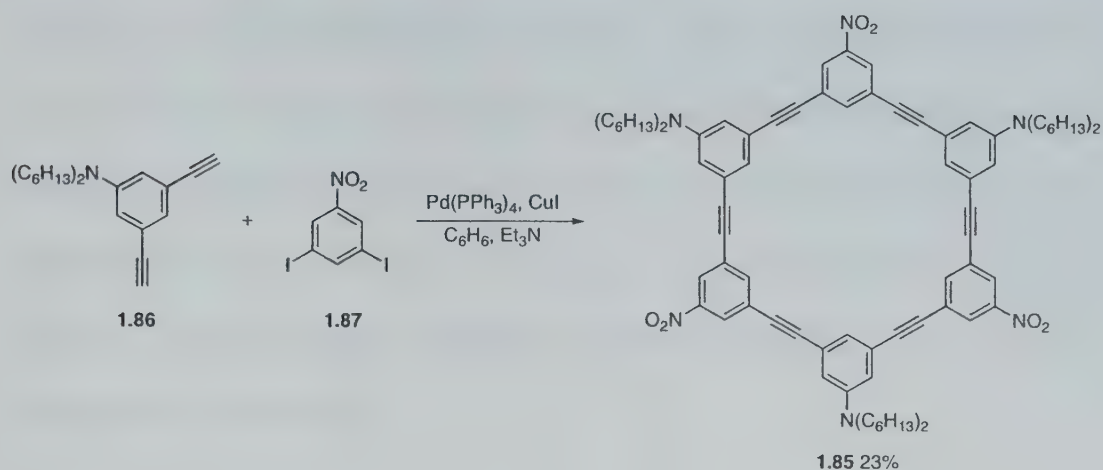
Scheme 1-13 Attempted synthesis of **1.78** from **1.79**



Scheme 1-14 Synthesis of HPEB derivative **1.80**

In 2005, Gleiter and coworkers³⁸ reported the synthesis of donor-acceptor-substituted phenylacetylene macrocycle (PAM) **1.85** using a one-pot reaction under high-dilution conditions (Scheme 1-15). Compound **1.86** was reacted with **1.87** via Sonogashira cross-coupling to yield **1.85** in 23% yield. It is noteworthy that the synthesis of the analog of **1.85** containing 4-*N,N*-diethylanilino instead of 4-*N,N*-dihexylanilino groups was

attempted but the product had low solubility which in turn hindered its purification and characterization.³⁸



Scheme 1-15 Synthesis of D-A PAM **1.85**

1.3 Conclusions

In this chapter, the use of the TEE and phenylacetylene scaffolding to synthesize 2D-conjugated molecules and oligomers bearing donors and/or acceptor substituents has been described. Although both TEE and phenylacetylene molecular scaffolding are very efficient, they still suffer from synthetic drawbacks, such as the formation of undesired oligomers, which make purification challenging. Considerable progress toward improvement of the stability and solubility of these push-pull chromophores has nevertheless been made. To this end, one of the main goals of this thesis has been to develop a viable synthetic strategy toward the incorporation of electron-donating and withdrawing substituents about a 2D-conjugated framework.

The second goal of this research relates to the study and establishment of structure-property relationships of the resulting donor and/or acceptor substituted molecules. The ideal chromophore is envisioned to be one that possesses a 2D-conjugated framework of low symmetry and bearing donor and acceptor substituents. These factors are expected to afford smaller HOMO-LUMO gaps which in turn would be suitable third-order NLO materials with the potential to be used in optoelectronic devices.^{4,6}

1.4 References and notes

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Chapter 2 Synthesis of donor and/or acceptor cross-conjugated macrocycles

2.1 Introduction

The Tykwinski group has been actively involved in the synthesis and study of acyclic and cyclic cross-conjugated molecules for more than a decade. This work initiated with the first example of an expanded radialene (Figure 2-1) based on an enyne building block.¹ Dr. Sara Eisler, a former Ph.D. student, successfully developed a viable synthetic route toward various members of the family of expanded radialenes (**[*n*]ERs**) containing an acetylene unit as the π -spacer in the cyclic framework.¹

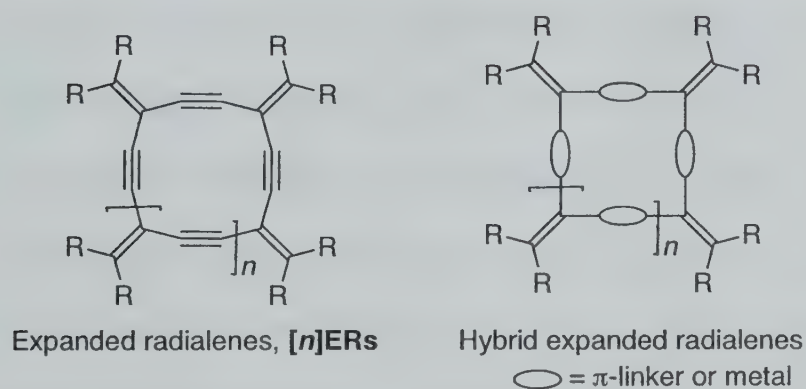


Figure 2-1 Schematic representation of ERs and hybrid ERs

This strategy, which relied heavily on the Sonogashira reaction² to assemble the conjugated core, was later used by another former member of our group, Dr. Katie Campbell, to assemble the so-called hybrid radialenes (Figure 2-1) that featured increased solubility and stability.³ This general synthetic protocol has been recently refined by Dr. Mojtaba

Gholami, to synthesize a series of perphenylated expanded radialenes, and these derivatives displayed even better solubility and stability characteristics during the purification and characterization.⁴ One fact that has become clear during the course of these studies is the fact that the refined synthetic strategy is particularly successful in producing the perphenylated **[4]ER** (R = Ph), both in terms of reaction yields and product stability, e.g., **[4]ER** (R = Ph) exhibited remarkable thermal stability, with a melting point above 305 °C.^{4a} The scope of this method has been further expanded to include **[4]ERs** with other functional groups about the periphery.^{4d}

Two-dimensionally conjugated (*2D*) frameworks containing electron-donating and –withdrawing substituents are known to be electronically interesting and potentially useful as nonlinear optical materials.⁵ Even so, to date there are very few examples that allow systematic incorporation of donor (D) and acceptor (A) substituents onto a *2D* skeleton. The two most common and versatile molecular platforms are the tetraethynylethenes (TEEs)⁶ and tetrakis(phenylethynylbenzenes) TPEBs⁷ (see Figure 1-2). The scarcity of viable synthetic routes toward the systematic placement of donors and acceptors into *2D*-conjugated frameworks has been the source of motivation for the work described in this chapter. The **[4]ER** was viewed as an alternative *2D*-conjugated platform for appending D and/or A groups to afford multipolar *2D*-conjugated chromophores. It was envisioned that if a viable synthetic

strategy to synthesize the donor and/or acceptor substituted radialenes could be found, the electronic, optical as well as NLO properties of these molecules could be explored. The ultimate goal of this project would be a [4]ER with an optimized of third-order NLO response for application(s) in optoelectronic devices.

Much like the D/A substituted TEEs reported by Diederich and co-workers in the 1990s,⁶ it was envisioned that the orientation of donor/acceptor substituents about the [4]ER framework, as well as the degree of substitution, would influence the optoelectronic properties of these systems. In terms of substitution patterns [4]ERs offer both symmetrical and unsymmetrical arrangements of the donor and acceptor; both of which are important to the establishment of structure-property relationships. A schematic representation of possible targets based on degree and pattern of substitution in a [4]ER is shown in Figure 2-2.

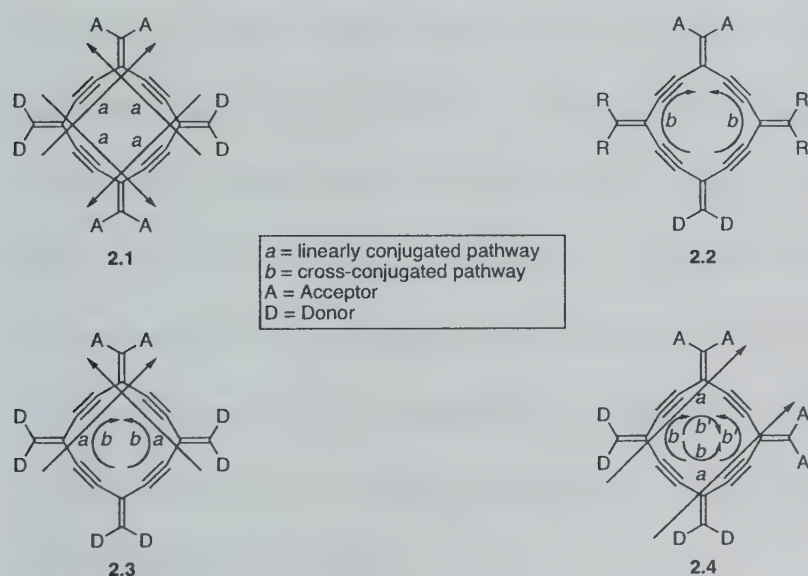
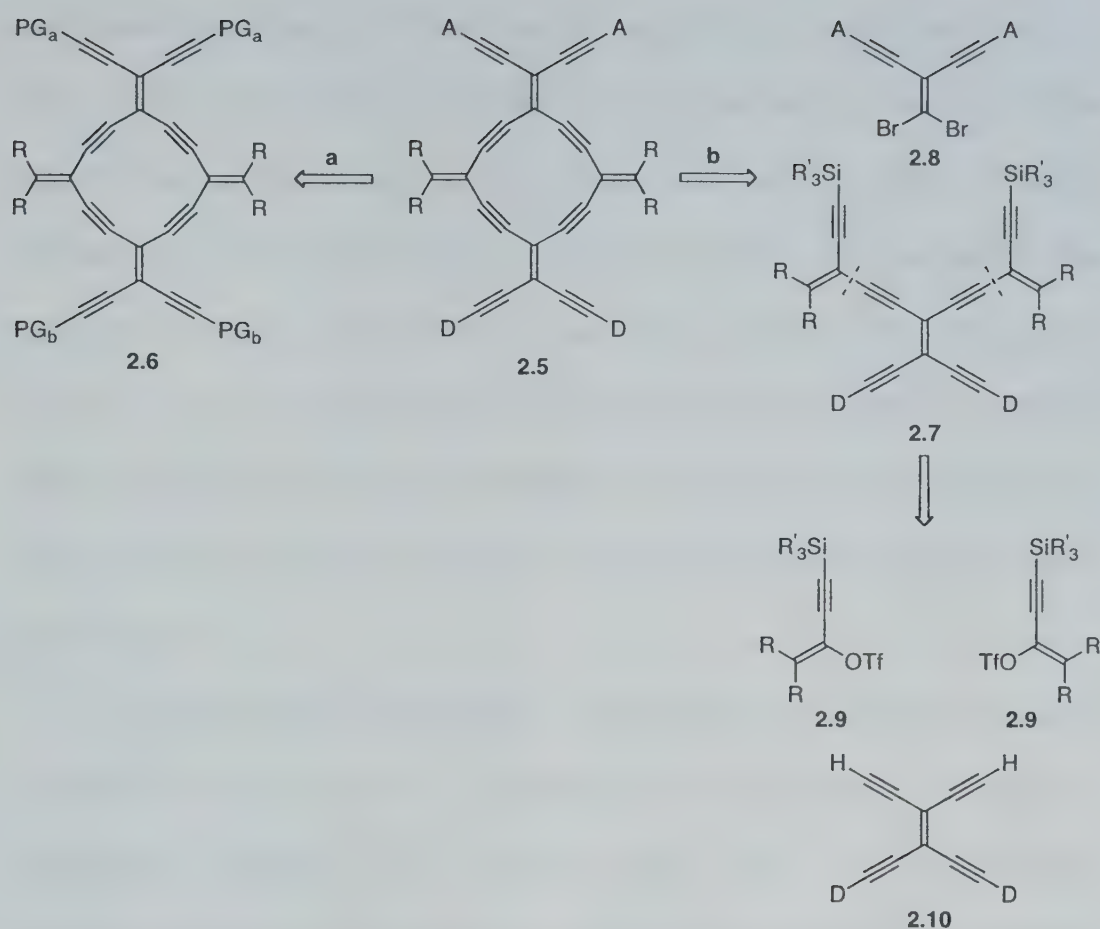


Figure 2-2 Schematic representation of some donor-acceptor interactions that are possible using the [4]ER framework

Radialene **2.1** (Figure 2-2) features four linearly conjugated pathways (*a*) between donor and acceptor alkylidene units, while **2.2** shows only two cross-conjugated pathways (*b*). By changing the degree and symmetry of D/A substitution about the periphery of the radialene, other possible targets in this series are arrived at via various combinations of paths *a* and *b*, e.g., **2.3** shows two linearly- and two cross-conjugated interactions, and **2.4** shows two linearly- and four cross-conjugated interactions.

In principle, the synthetic strategy developed in the Tykwinski group facilitates the construction of the [4]ERs **2.5** in two different ways (Scheme 2-1). The first method (route **a**) relies on the use of orthogonal alkyne protecting groups (PG_a and PG_b) to assemble and decorate the radialene core of **2.6**. These PGs can then be selectively removed to give the desired D/A radialene **2.5**. The other approach (route **b**) incorporates the use of building blocks with the donor and/or acceptor functionalities already in place, e.g., trimer **2.7** reacting with a dibromoolefin **2.8** to give **2.5** directly. Disconnection of the bonds shown in **2.7** then gives rise to two key building blocks, vinyl triflate **2.9** and terminal enediyne **2.10**. Conveniently, **2.10** can typically be prepared from a dibromoolefin (e.g., **2.8**) via Sonogashira cross-coupling with the terminal alkyne.⁸ The method used to assemble the [4]ERs synthesized in this Thesis is, more or less, a hybrid of these two routes.



Scheme 2-1 Retrosynthesis of [4]ERs 2.5

The key to the synthetic pathway outlined in Scheme 2-1 is, thus, the formation of vinyl triflates such as **2.9**, which serve as the electrophilic coupling partner in the Sonogashira reaction. Vinyl triflates have been specifically chosen because they can be effectively used as cross-coupling partners in the Sonogashira reaction. In addition, they are readily synthesized from the corresponding ketone through reaction with base to form the enolate and subsequent trapping with triflic anhydride. The skillful choice of alkynyl protecting groups offers synthetic flexibility, and, finally vinyl triflates allow for variation of physical properties by simply changing

the appended group(s).^{4c} The use of vinyl triflates in the assembly of cross-conjugated oligomers and macrocycles has been aided through the development of a one-pot reaction to gain access to a variety of highly functionalized vinyl triflates from the corresponding vinyl acetates.⁹ This divergent synthetic route was successfully used to form ethynylated, arylated, and heteroarylated vinyl triflates in good to excellent yields. The ability to express different functionalities on the vinyl triflate provides the opportunity to tune the properties of the highly conjugated systems derived from it.

Notably absent from the list of functionalized vinyl triflates reported in 2003⁹ were those that contained strongly electron-donating or -withdrawing groups, i.e., 4-nitrophenyl and 4-*N,N*-dialkylanilino derivatives. It is noteworthy that the 4-nitrophenyl and 4-*N,N*-dialkylanilino groups have been chosen particularly because they can be easily incorporated into a synthetic strategy using readily available precursors, and, more importantly, they are established as good electron-acceptor and donor, respectively.^{3f} The first goal of my project was, therefore, to expand the scope of this one-pot procedure and gain access to even more densely functionalized *iso*-PDAs **2.7** through the incorporation *N,N*-dialkylanilino substituents into the vinyl triflate building block **2.9**. The synthesis of a vinyl triflate cross-coupling partner **2.9** containing electron-withdrawing groups was also considered, but this idea was dismissed due to potential solubility and stability issues, as well as the lack of precedent.

More specifically, the *N,N*-diisopropylanilino groups were chosen because it was previously reported that they enhance solubility, augment stability in comparison to the *N,N*-dimethylanilino substituted derivatives, and have a pronounced effect on the electronic make-up of the resulting π -conjugated systems.¹⁰

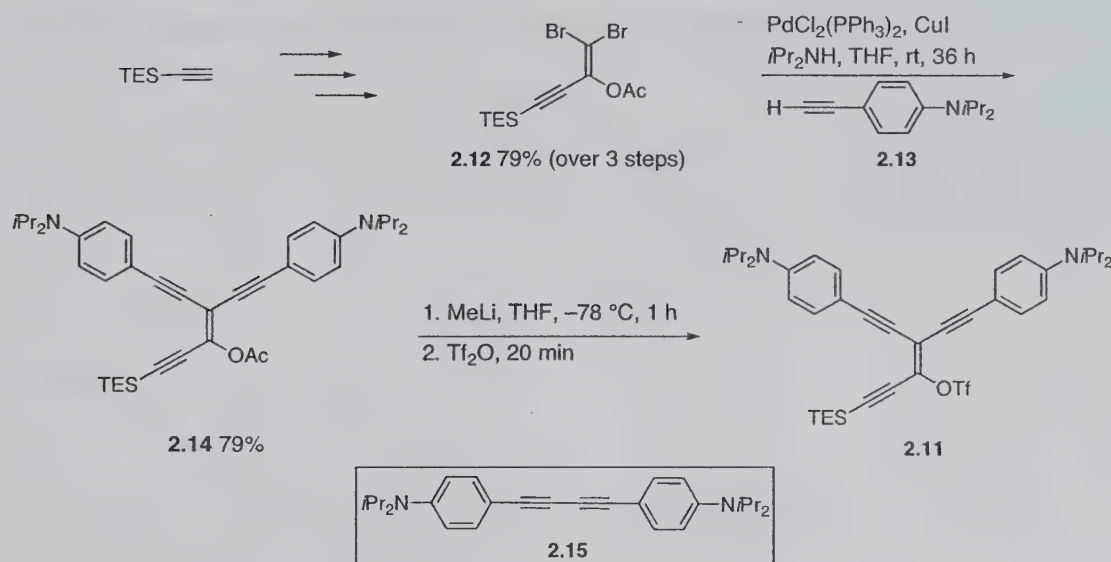
The work described in this chapter covers the synthetic efforts toward the acquisition of the so-called “molecular construction kit”^{8c} for use in the “oligomer approach”¹¹ toward the assembly of *iso*-PDAs and **[4]ERs**. First, the synthesis of the three main classes of building blocks for the assembly of the **[4]ERs** is described: (1) the vinyl triflates, (2) the dibromoolefins, and (3) the TEEs. The remainder of the chapter will address the use of the *iso*-PDAs precursors in the construction of D/A substituted **[4]ERs**. It is noted that spectroscopic evidence for the formation of the building blocks is outlined here, while that of the **[4]ERs** will be given more attention in Chapter 3, which deals with structure-property relationship studies.

2.2 Synthesis of building blocks

2.2.1 Synthesis of vinyl triflates

The assembly of the **[4]ERs** began with the synthesis of the key building block, vinyl-triflate **2.11** from vinyl acetate **2.12** (Scheme 2-2). Compound **2.12** was synthesized in three steps from TES-acetylene with an overall yield of 79% using the procedure reported by Rankin and

Tykwinski.⁹ Protodesilylation of **2.13** using K_2CO_3 followed by Sonogashira cross-coupling with dibromovinyl acetate **2.12** provided anilino vinyl acetate **2.14** after FCC in 79% yield as a bright yellow foam. Separation of the desired vinyl acetate **2.14** and the product of oxidative homocoupling side-reaction, **2.15** was not trivial because of their nearly identical polarities and was exacerbated by the limited solubility of **2.15**.

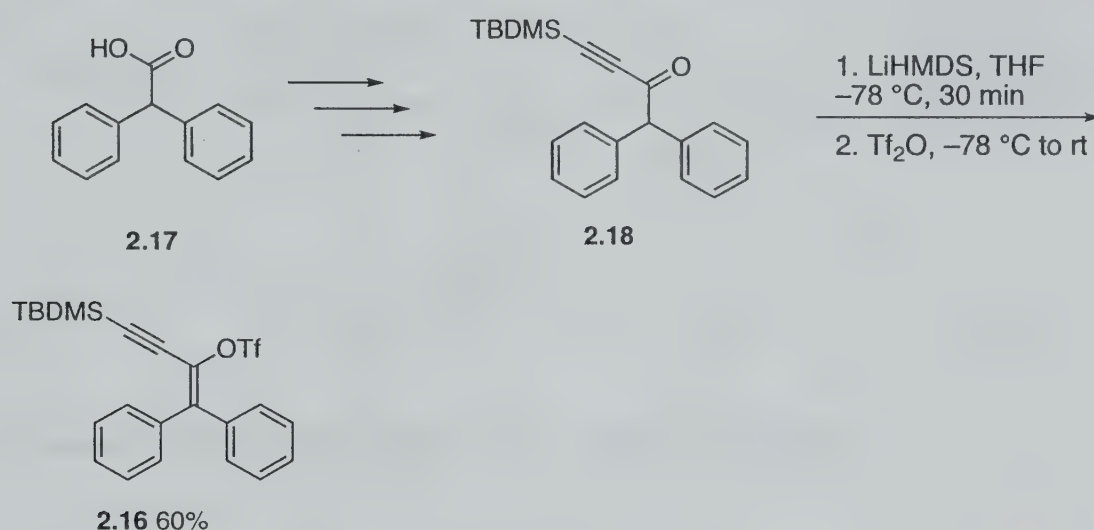


Scheme 2-2 Synthesis of vinyl triflate **2.11**

The data obtained from 1H and ^{13}C NMR, and IR spectroscopies are consistent with the proposed structure of vinyl acetate **2.14**. Additional evidence for this structure was provided by ESI-MS and EA.

Treatment of vinyl acetate **2.14** with two equivalents of MeLi for 1 h followed by the addition of two equivalents of Tf_2O at $-78\text{ }^\circ\text{C}$ in THF provided crude vinyl triflate **2.11** after filtration through a short plug of silica gel using EtOAc/hexanes (ca. 1:19) as the eluent in nearly quantitative yield as a dark yellow oil. Although the formation of **2.11** appeared to be

quite successful, as the reaction proceeded under the standard reaction conditions, the product **2.11** was not sufficiently stable for isolation and complete characterization. Nevertheless, ^1H NMR and ESI mass spectra obtained for the crude product **2.11** were sufficient evidence for its formation to move forward with the synthetic plan. Thus, compound **2.11** has always been made immediately prior to each Sonogashira cross-coupling reaction and used without further purification.

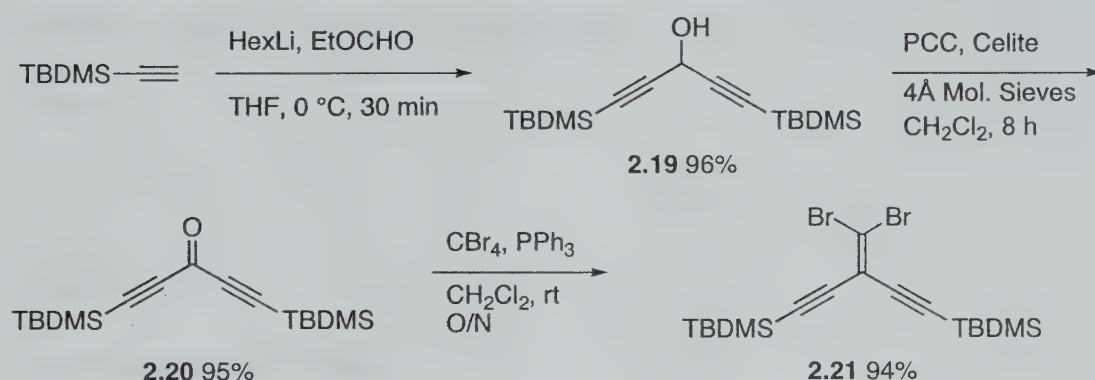


Scheme 2-3 Synthesis of vinyl triflate **2.16**

Another useful vinyl triflate **2.16** (Scheme 2-3), whose synthesis is well known in the group, was formed as described in Scheme 2-3. Briefly, diphenylacetic acid **2.17** was converted by a known procedure to ketone **2.18**.¹² Reaction of **2.18** with LiHMDS followed by trapping of the enolate with Tf_2O afforded compound **2.16** in 60% yield as a yellow oil. The spectral data obtained for this compound are consistent with that reported.¹²

2.2.2 Synthesis of dibromoolefins

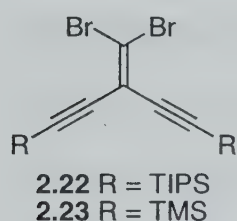
The second class of building blocks that was targeted was the dibromoolefins **2.8**. Dibromoolefins are very versatile not only because they serve as key building blocks in the assembly of the [4]ERs, but are also progenitors of the TEEs. The synthesis of dibromoolefins is well established in the literature¹³ and a representative example of their synthesis is shown in Scheme 2-4.



Scheme 2-4 Representative synthesis of a dibromoolefin (**2.21**)

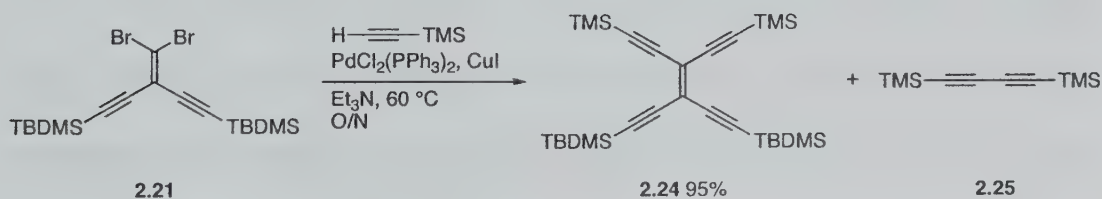
TBDMS-acetylene was lithiated at 0° C via treatment with 2.3 M hexyllithium (Scheme 2-4). The resulting lithium acetylide was trapped with ethyl formate and compound **2.19** was isolated in nearly quantitative yield. Alcohol **2.19** was oxidized using PCC to the corresponding ketone **2.20** in excellent yield. Ketone **2.20** was then converted to the corresponding 3-(dibromomethylidene) derivative **2.21** in excellent yield using the Ramirez¹² reaction conditions. Evidence to support the proposed structure of **2.21** has been provided by ¹H NMR, ¹³C NMR and IR spectroscopies, as well as HR mass spectrometry and EA.

Two other key dibromoolefins were assembled using the same protocol as has been described in the literature.^{8b} The more robust TIPS-substituted 3-(dibromomethylidene) derivative **2.22** was synthesized in excellent yield over three-steps with purification being done in the final step of the synthetic sequence. The more labile bis(trimethylsilyl) derivative **2.23** was synthesized in modest yield under the identical conditions used for **2.21**. The spectral data of **2.22** and **2.23** were consistent with that previously reported.^{8b}



2.2.3 Synthesis of TEEs

As mentioned earlier, the dibromoolefins are precursors to tetraethynylethenes. Orthogonally protected TEEs are of particular interest because they facilitate further functionalization subsequent to their introduction into a synthetic sequence. A representative synthesis of a TEE from the corresponding dibromoolefin is shown in Scheme 2-5.

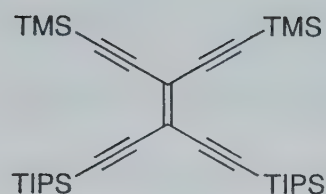


Scheme 2-5 Formation of the orthogonally protected TEE **2.24**

Dibromoolefin **2.21** was subjected to a Sonogashira cross-coupling reaction at 60 °C with excess trimethylsilylacetylene (four equivalents) to produce the orthogonally protected TEE **2.24** (Scheme 2-5) in nearly quantitative yield as a light-brown solid after FCC using hexanes as the eluent. This reaction was initially done under the conditions reported by Anthony et al.^{8b} but was found to be too sluggish, the yields were poor, and purification was tedious due to the similar polarities of the by-product, 1,4-bis(trimethylsilyl)butadiyne **2.25**, and the desired TEE. The only real modifications of the published procedure was that *n*-butylamine was replaced with triethylamine, and the reaction was performed at 60 °C instead of at room temperature.

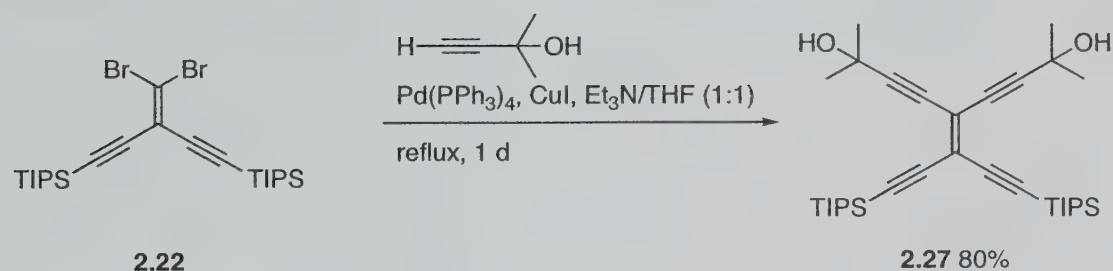
The spectral data obtained using ¹H NMR, ¹³C NMR and IR spectroscopies as well as HR mass spectrometry and EA support the proposed structure for TEE **2.24**. The notable appearance of two new signals in the sp-region of the ¹³C NMR spectrum was a key piece of evidence supporting the successful conversion of a dibromoolefin to a TEE.

The TIPS/TMS protected TEE **2.26** was synthesized in excellent yield in an analogous manner to **2.24** and was purified via two-solvent recrystallization with CH₂Cl₂/MeOH at 5 °C. The spectral data for **2.26** are consistent with that previously reported.^{8b}



2.26

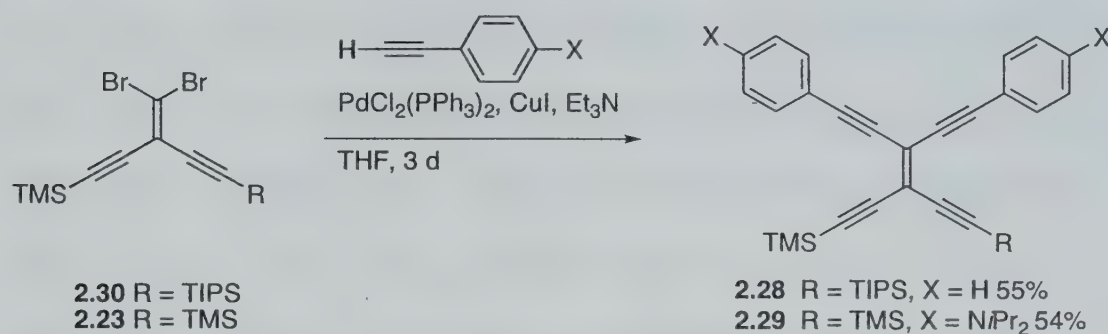
The synthesis of another important orthogonally protected TEE was developed from the corresponding TIPS-substituted dibromoolefin **2.22** as described in Scheme 2-6. The motivation for the synthesis of compound **2.27** was based on the following: (1) the selective removal of the acetonide in the presence of the TIPS protecting group could be exploited in the synthesis of the desired radialenes, and (2) the presence of the acetonide groups should substantially aid the chromatographic purification process due to the presence of alcohol functional groups. With these factors in mind, compound **2.27** was synthesized via Sonogashira cross-coupling and isolated after FCC (silica gel, EtOAc/hexanes 1:4) in 80% yield as a colorless solid.



Scheme 2-6 Synthesis of an acetonide-TIPS substituted TEE **2.27**

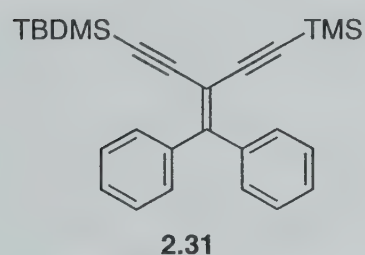
Arylated TEEs **2.28** and **2.29** (Scheme 2-7) were also synthesized in satisfactory yields from dibromoolefins **2.30** and **2.23**, respectively using known procedures.^{8c} These reactions were easily monitored by TLC

because the highly conjugated TEEs are brightly colored and fluoresce under the 365 nm irradiation using a UV lamp. The spectral data of **2.28** are consistent with that previously reported.^{8c} The spectral data obtained using ¹H NMR, ¹³C NMR and IR spectroscopies as well as HR mass spectrometry and EA support the proposed structure for **2.29**.



Scheme 2-7 Synthesis of arylated TEEs

Finally, the synthesis of the orthogonally protected arylated *gem*-diethynylethene (DEE) **2.31** is well known in the group and was synthesized according to the literature procedure.¹²



2.3 Synthesis of cross-conjugated oligomers and [4]ERs

2.3.1 Synthesis of cross-conjugated oligomers and [4]ERs based on vinyl triflate 2.11¹⁶

The initial series of [4]ERs targeted was based on the use of the vinyl triflate **2.11** and are shown in Figure 2-3. Compound **2.32** is the precursor to D-A substituted [4]ER **2.33** while **2.34** is a progenitor to the D-A substituted [4]ER **2.35**. It is noteworthy that this represents the very first attempt to use such a highly functionalized vinyl triflate in the assembly of [4]ERs. This series of molecules offers the opportunity to explore structure-property relationship studies based on the degree of substitution about the radialene core.

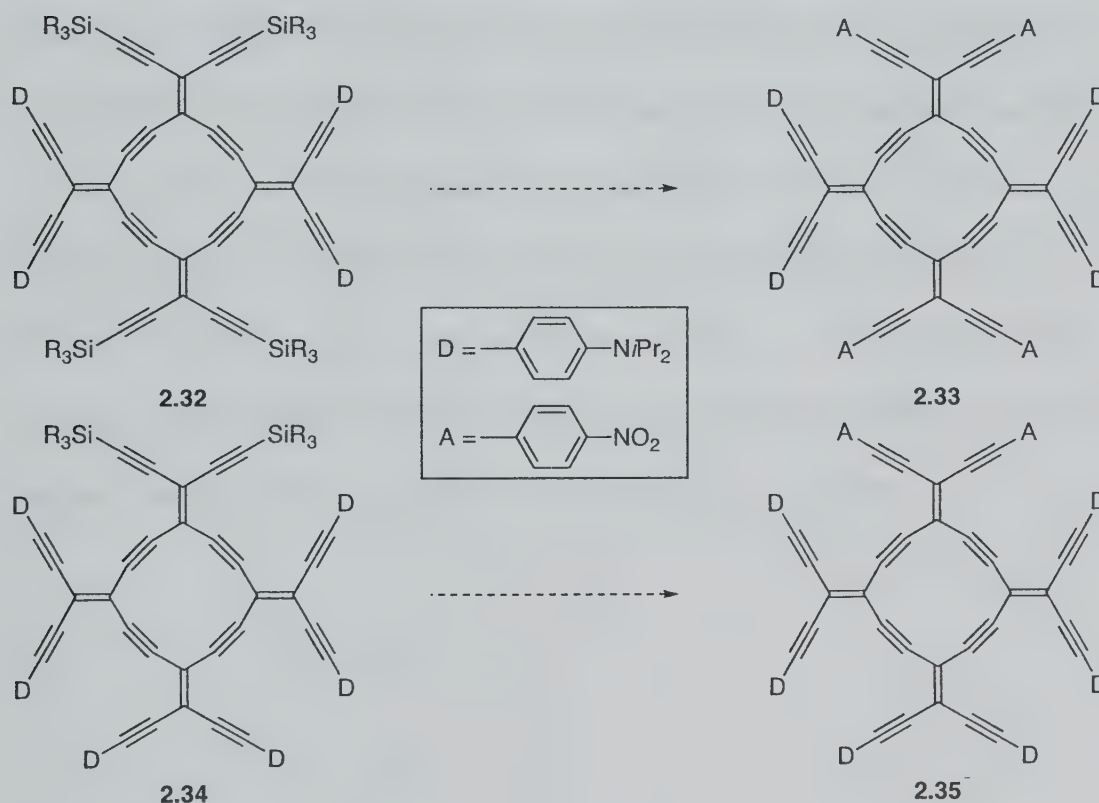
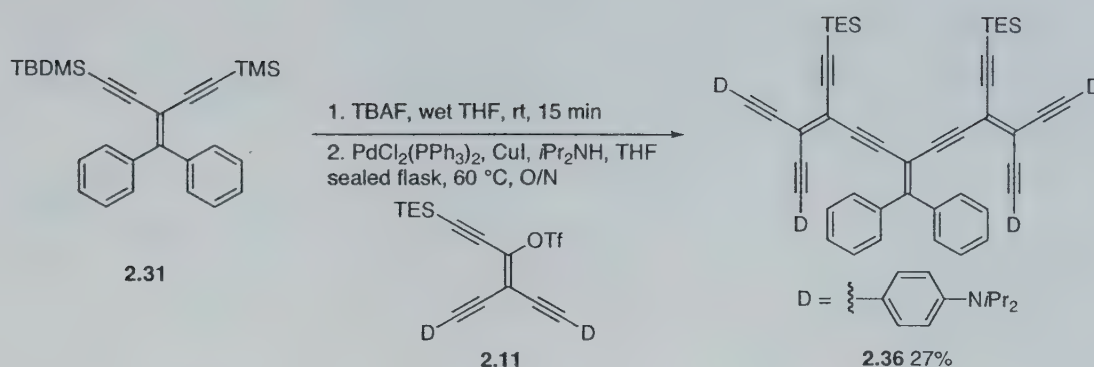


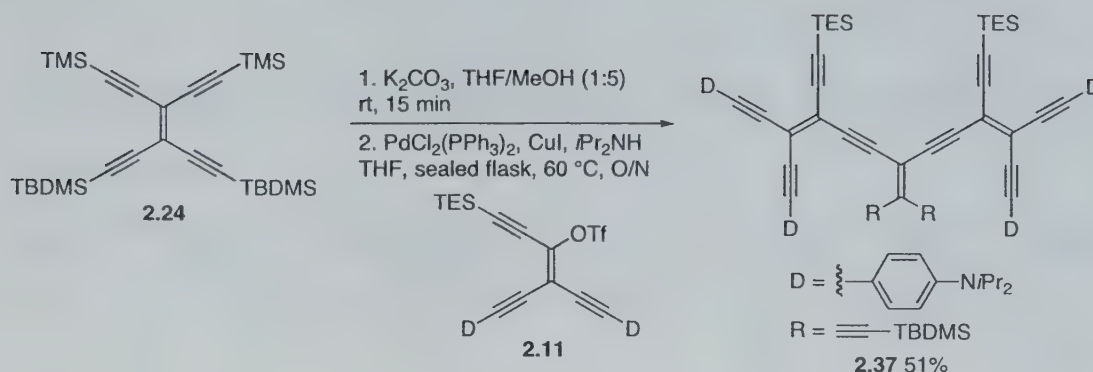
Figure 2-3 Initial [4]ERs targets

Encouraged by the successful use of the arylated *gem*-DEE **2.31** in the synthesis of *iso*-PDAs¹² and **[4]ERs**,^{4a} model compound **2.36** was targeted (Scheme 2-8). Desilylation of compound **2.31** using TBAF at rt for 2 h followed by aqueous work-up yielded the terminal diyne which was used in the subsequent step without further purification. Taking careful measures to exclude oxygen, the terminal diyne was reacted with three equivalents of the electron-rich vinyl triflate via Sonogashira cross-coupling at 60 °C overnight (O/N) to afford the desired *iso*-PDA **2.36**¹⁶ after FCC in a modest yield of 27%. After a significant amount of trial and error, TLC analysis revealed the presence of numerous spots with similar *R_f* values. Thus, purification of **2.36** was not a trivial task. The formation of several by-products in this reaction was attributed to the presence of adventitious oxygen that increases the amount of homocoupling side-products and significantly lowers the yield of the reaction. Purification of this oligomer was exacerbated by the nearly identical polarities of the desired compound and side-products formed in this reaction. The presence of four tertiary amino groups may also be responsible for loss of product due to strong interactions with the silica gel support.



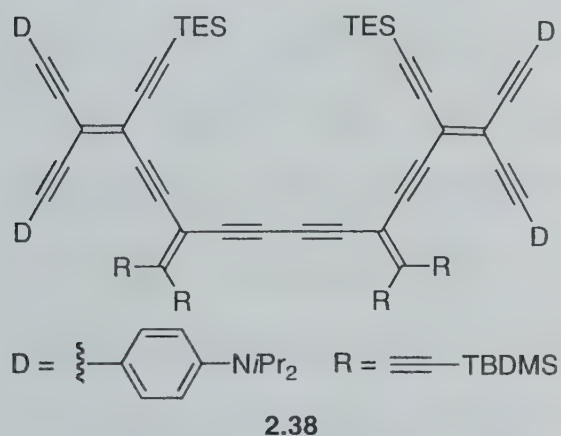
Scheme 2-8 Synthesis of model compound **2.36**

Encouraged by the modest success in synthesizing **2.36** the preparation of an orthogonally protected *iso*-PDA **2.37** was undertaken (Scheme 2-9). Selective removal of the TMS groups of **2.24**, followed by aqueous work-up, provided the terminal diyne, which was then reacted with vinyl triflate, **2.11** to produce *iso*-PDA **2.37** as a dark red solid in 51% yield. Despite all efforts to exclude oxygen by rigorously bubbling argon through the solvents used and performing the reaction in a sealed flask under argon, oxidative homocoupling of the terminal acetylene in these reactions was still a problem. Consequently, separation of the orthogonally protected *iso*-PDA **2.37** from the oxidatively homocoupled by-products was complicated by their nearly identical polarities, which was also the reason recrystallization was not used. Among the methods used for the characterization of **2.37** are IR and ^1H NMR and ^{13}C NMR spectroscopies, which will be discussed in more detail in Chapter 3.



Scheme 2-9 Synthesis of orthogonally protected *iso*-PDA **2.37**

Although many products were formed in the synthesis of **2.37**, most were present in small amounts. In one case, however, sufficient material was available to use ^1H and ^{13}C NMR spectroscopies to confirm the structure of one of the oxidatively homocoupled by-product **2.38**.



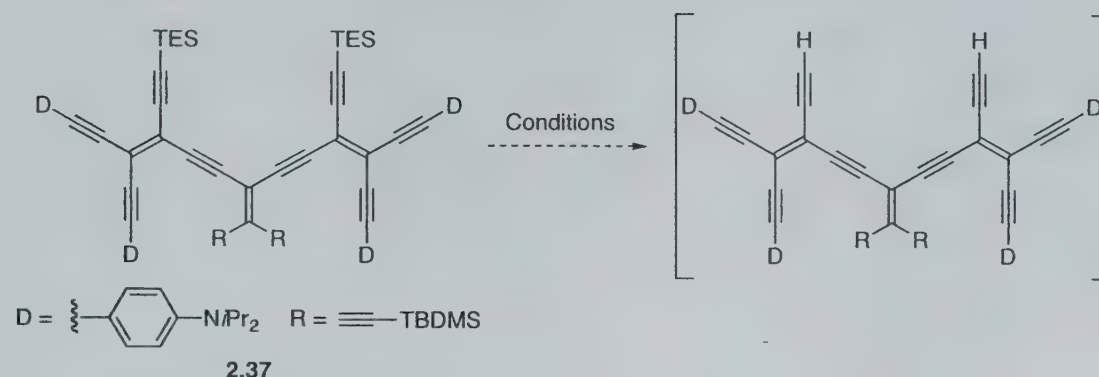
Employing catalysts typically available and used successfully in the Tykwinski laboratory at the time (i.e., $\text{Pd}(\text{PPh}_3)_4$ and $\text{PdCl}_2(\text{PPh}_3)_2$), an effort was made toward the optimization of this reaction. The results are summarized in Table 2-1. One will notice immediately that there was no real trend but that the conditions indicated in entry 3 were found to be best for this particular system.

Table 2-1 Summary of the conditions employed toward the optimization of the synthesis of **2.37**

Entry	Pd(PPh ₃) ₄ /mol%	PdCl ₂ (PPh ₃) ₂ /mol%	CuI /mol%	Temp /°C	Yield %	Time
1	—	10	15	25	19	3.5 d
2	—	10	15	60	40	O/N
3	—	5	10	60	51	O/N
4	5	—	10	25	12	3 d
5	5	—	10	60	22	O/N

Radialene formation using orthogonally protected *iso*-PDA **2.37** required the selective removal of the TES groups in the presence of the TBDMS protecting groups (Table 2-2). Unfortunately, the use of typical conditions to accomplish this feat (treatment with 1 M NaOH_(aq) in THF/MeOH) at room temperature led to the formation of a complex mixture. Similar results were obtained when the desilylation was attempted using K₂CO₃ in THF/MeOH at room temperature or at reflux. Even more devastating results were obtained when this selective deprotection was done using 1 M TBAF at –78° C in wet THF. Based on TLC analysis, only baseline material (i.e. the spot does not elute) was observed upon addition of TBAF. A summary of the conditions and the corresponding results obtained during attempts to selectively remove the TES group are given in Table 2-2.

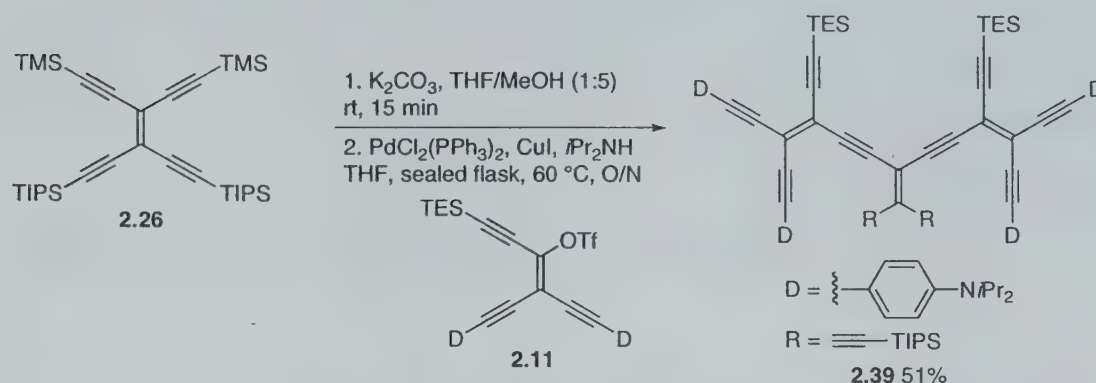
Table 2-2 Summary of the conditions and results for selective removal of the TES groups of **2.37**



Conditions	Temp	Time	Results
1M NaOH (aq) THF/MeOH (1:1)	rt	4 h	Complex mixture
K ₂ CO ₃ THF/MeOH (1:5)	rt	24 h	Complex mixture
K ₂ CO ₃ THF/MeOH (1:5)	reflux	6 h	Complex mixture
TBAF, wet THF	−78 °C	5 min	Baseline material

At this stage, the orthogonally protected *iso*-PDA target was redesigned such that TBDMS groups were replaced with the TIPS protecting groups. The latter was chosen based on the fact that there was precedent in our group where the TIPS protecting group, while more expensive, proved to be more robust than the TBDMS and therefore easier to use. Consequently, compound **2.39** was synthesized in a manner analogous to compound **2.37**; and the product was isolated using FCC in 37% yield as a dark-red solid (Scheme 2-10). The proposed structure for compound **2.39** was supported by HR MALDI mass

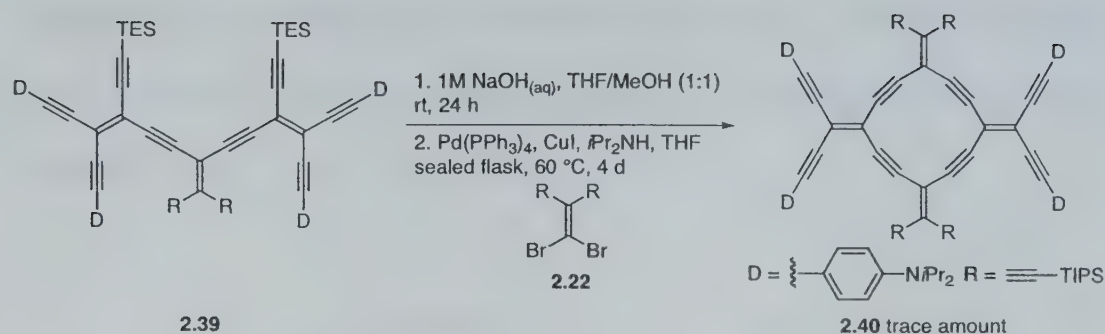
spectrometry, NMR, and IR spectroscopies. Further discussion of the spectroscopic data of this compound will be given in Chapter 3.



Scheme 2-10 Synthesis of orthogonally protected *iso*-PDA **2.39**

Selective removal of TES groups in the presence of TIPS protecting groups of *iso*-PDA **2.39** was accomplished through reaction with 1 M $\text{NaOH}_{(\text{aq})}$ and THF/MeOH as the solvent. Based on TLC analysis, the reaction was relatively cleaner compared to when the identical reaction used for compound **2.37**. Following aqueous work-up, the desilylated oligomer was passed through a short plug of silica gel using EtOAc/hexanes (1:4) as the eluent to yield a black residue, which was used in the next step without further purification.

Radialene formation to give **2.40** was attempted under the conditions given in Scheme 2-11. It was possible to detect **2.40** by low-resolution MALDI mass spectrometry and ^1H NMR spectroscopy as a component of an impure fraction. All efforts to isolate and purify sufficient material for characterization were futile.

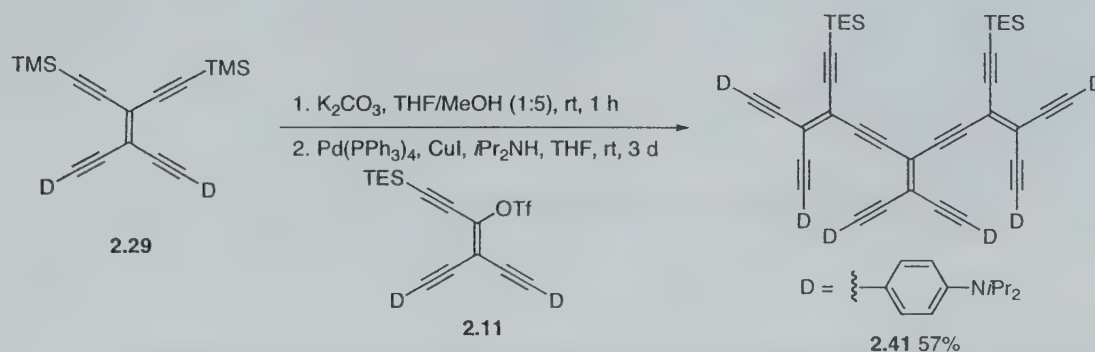


Scheme 2-11 Attempted formation of a symmetrical [4]ER

Attention was then turned to a system that did not require selective removal of trialkylsilyl protecting groups in the penultimate step, namely **2.41** (Scheme 2-12). Protidesilylation of the arylated TEE **2.29** followed by Sonogashira cross-coupling with vinyl triflate **2.11** afforded *iso*-PDA **2.41** after FCC in 57% yield as a black solid. Characterization of the highly electron-rich *iso*-PDA **2.41** was done using the same tools used for the previously synthesized analogs and will be given more attention in Chapter 3. The slightly improved isolated yield of compound **2.41** may be attributed to the fact that separation of the reaction mixture by FCC was mitigated by the presence of the tertiary anilino groups although they may also be responsible for the loss of some product due to the strong interactions with the silica gel support.

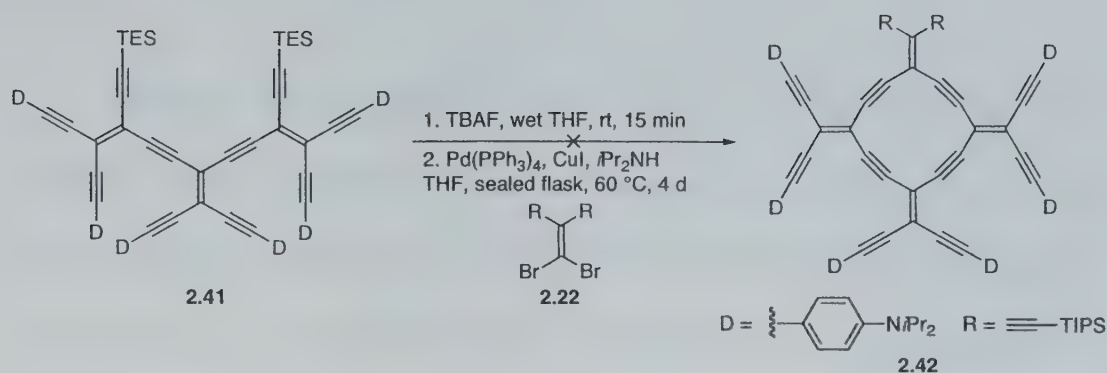
After careful inspection of the reaction conditions used for the synthesis of *iso*-PDA **2.41**, one will notice that the more active Pd(PPh₃)₄ (pre)catalyst was used and that the reaction was performed at room temperature for a longer period of time. Any effort to perform this reaction using PdCl₂(PPh₃)₂ as a catalyst, under the conditions used for the

synthesis of the orthogonally protected *iso*-PDA **2.37**, led more complex reaction mixtures that were difficult to purify, which in turn led to lower isolated yields.



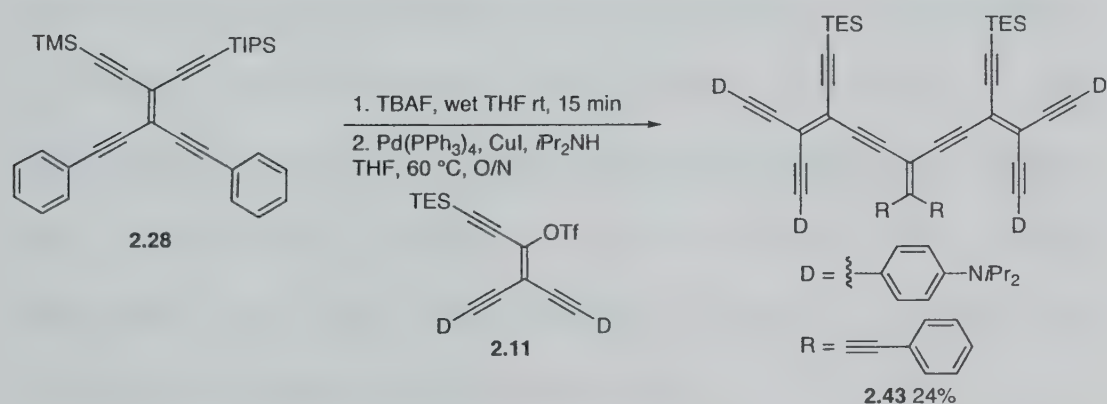
Scheme 2-12 Synthesis of *iso*-PDA **2.41**

The desilylation of *iso*-PDA **2.41** proceeded smoothly as evidenced by TLC analysis, and no signs of decomposition were observed during the aqueous work-up and concentration steps. Following the successful removal of the TES groups, the desilylated product was carried on to radialene formation with **2.22** at 60 °C under the reaction conditions shown in Scheme 2-13. Unfortunately, the reaction was not successful. After four days, nearly all of the dibromoolefin **2.22** and only a trace amount of the desired radialene **2.42** were observed as an inseparable mixture upon isolation.



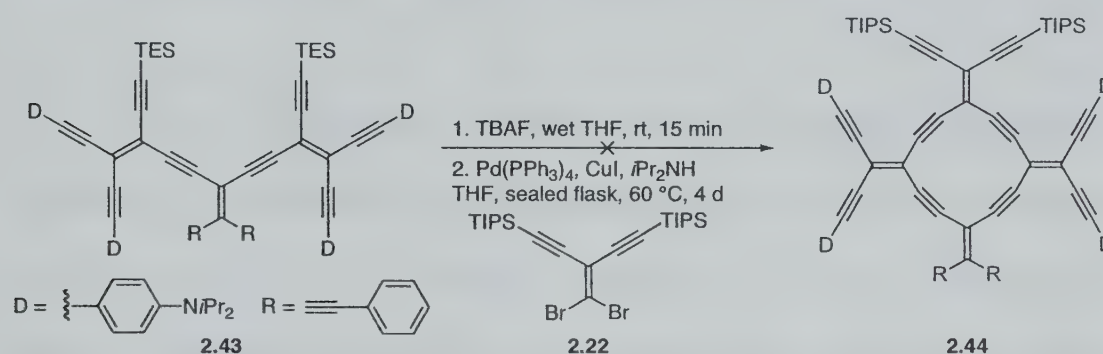
Scheme 2-13 Attempted radialene formation using *iso*-PDA **2.41**

Motivated by the modest success in producing *iso*-PDA **2.41** in reasonable quantities, the less-densely functionalized *iso*-PDA **2.43** (Scheme 2-14) was targeted. Replacement of the *N,N*-diisopropylanilino with unsubstituted phenyl groups would still allow access to donor-acceptor substituted [4]ERs upon subsequent cyclization. Thus *iso*-PDA **2.43** was synthesized in an analogous manner to **2.41**. Exhaustive desilylation of TEE **2.28** with TBAF was followed by Sonogashira cross-coupling with vinyl triflate **2.11** under the conditions given in Scheme 2-14, to afford compound **2.43** after FCC in 24% yield as a dark red solid. Again, efforts to improve the outcome of this *iso*-PDA forming reaction were futile.



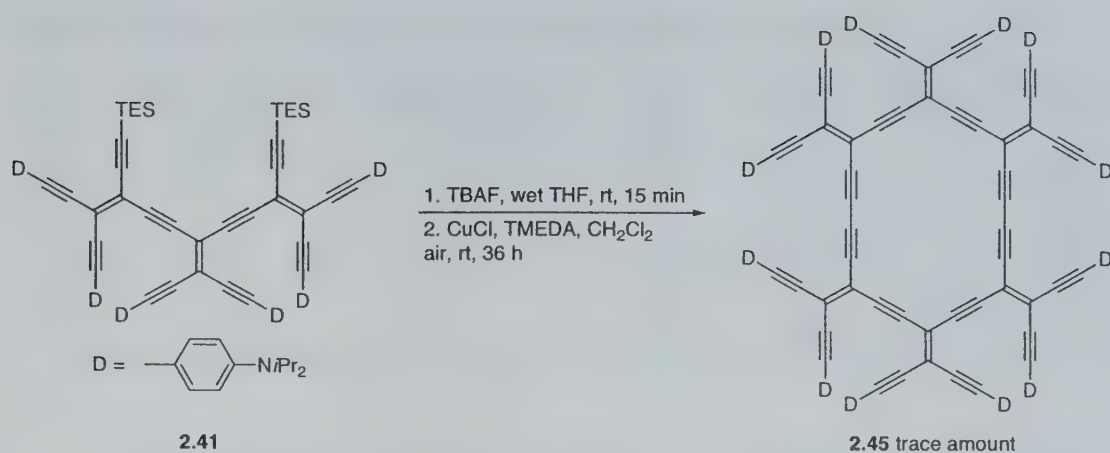
Scheme 2-14 Optimized synthesis of **2.43**

Attempts to desilylate *iso*-PDA **2.43** and cyclize onto the TIPS-substituted dibromoolefin **2.22** did not lead to the isolation of any of the desired [4]ER **2.44** (Scheme 2-15). Since nearly all of the dibromoolefin and none of the precursor *iso*-PDA were recovered, it was assumed that the latter was consumed in the competitive oxidative homocoupling reaction to produce larger acyclic oligomers and macrocycles.



Scheme 2-15 Attempted synthesis of [4]ER **2.44**

Before any further effort was put into the use of the electron-rich *iso*-PDAs for formation of [4]ERs, a modified, and procedurally simplified, reaction was performed to determine whether the resultant macrocyclic system should be sufficiently stable toward isolation and characterization. In this case, the Hay reaction¹⁴ was chosen because it is a well-established method for the formation of hybrid radialenes in the Tykwinski group.³ To this end, *iso*-PDA **2.41** was desilylated and oxidatively homocoupled under high-dilution conditions to favor the desired product **2.45** using the conditions given in Scheme 2-16.



Scheme 2-16 Synthesis of a hybrid radialene **2.45**

During the initial stages of the reaction, TLC analysis of the reaction indicated the formation of a single compound, assumed to be the desired hybrid radialene. As the reaction progressed, however, multiple spots began to appear on the TLC plate, possibly corresponding to larger macrocycles or linear oligomers. After the disappearance of the starting material, the reaction was subjected to aqueous work-up and yielded a purple residue after concentration. FCC (EtOAc/hexanes 1:5 → 1:1), removal of solvents, and washing of the solid residue with Et₂O led to the isolation of trace amounts of **2.45**. It was possible to detect the product **2.45** by low-resolution MALDI mass spectrometry as a component of the impure fraction, but because of poor stability and solubility it was not possible to isolate, purify and characterize the target molecule.

Table 2-3 Summary of optimized conditions for each *iso*-PDA

<i>Iso</i> -PDA	Pd(PPh ₃) ₄ /mol%	PdCl ₂ (PPh ₃) ₂ /mol%	CuI /mol%	Temp /°C	Yield %	Time
2.36	—	5	10	50-60	27	O/N
2.37	—	5	10	50-60	51	O/N
2.39	—	5	10	50-60	40	O/N
2.41	5	—	10	25	57	3 d
2.43	5	—	10	25	27	7 d

A summary of the optimized reaction conditions for each of the *iso*-PDAs synthesized using vinyl triflate **2.11** is given in Table 2-3. After inspecting these results, one will notice that the conditions used for the formation of the *iso*-PDAs are far from general, i.e., the conditions are specific for each *iso*-PDA and no real trends are apparent from the data. The reasons for this are not entirely clear. At first, it had been suspected that the presence of adventitious oxygen is responsible for the low isolated yields obtained for both the *iso*-PDAs and **[4]ERs**. Despite taking careful measure to deoxygenate solvents and performing the reaction under argon, reproducible results remain elusive, even with identical conditions and substrates. The next culprit might be the electron-rich vinyl triflate **2.11**, whose stability and reactivity has been brought into question. It had been believed for sometime that **2.11** was not stable to oxygen, heat, or light. Careful measures to exclude the influence of these environmental factors during reactions still failed to provide reproducible results.

In the case of radialene formation, the poor results might be attributed to the highly electron-rich nature and sterically demanding structures of the *iso*-PDAs. It is in fact, well-known in palladium catalyzed

alkynylations that electron-rich terminal alkynes perform poorly relative to their electron-poor counterparts.¹⁵ It is not yet clear, however, what role this fact plays in the present reactions.

Finally, purification of the *iso*-PDA products **2.36**, **2.37**, **2.39**, **2.41**, and **2.43** was often a tedious process that led to loss of precious material, which in turn prevented the accumulation of adequate material to move on with the synthesis. Since all efforts to synthesize, isolate and completely characterize ERs derived from vinyl triflate **2.11** were futile, the search for a viable route toward donor- and/or acceptor-substituted ERs continued.

2.3.2 Synthesis of oligomers and [4]ERs based on vinyl triflate **2.16**¹⁶

Attention was then turned to a less-densely functionalized system for which there was some synthetic precedent. As discussed earlier in this chapter, the modular synthesis of perphenylated systems such as *iso*-PDAs,¹² ERs,^{4a} bisradialenes^{4a,4c} and radiaannulenes^{4a-d} with reasonable stability and solubility properties has been established. This modular approach used primarily diphenyl vinyl triflate **2.16**, which was readily available in large quantities and can be stored for an extended period of time without loss due to degradation. With these factors in mind, model [4]ER **2.46** and its analogs **2.47-2.49** were targeted (Figure 2-4).

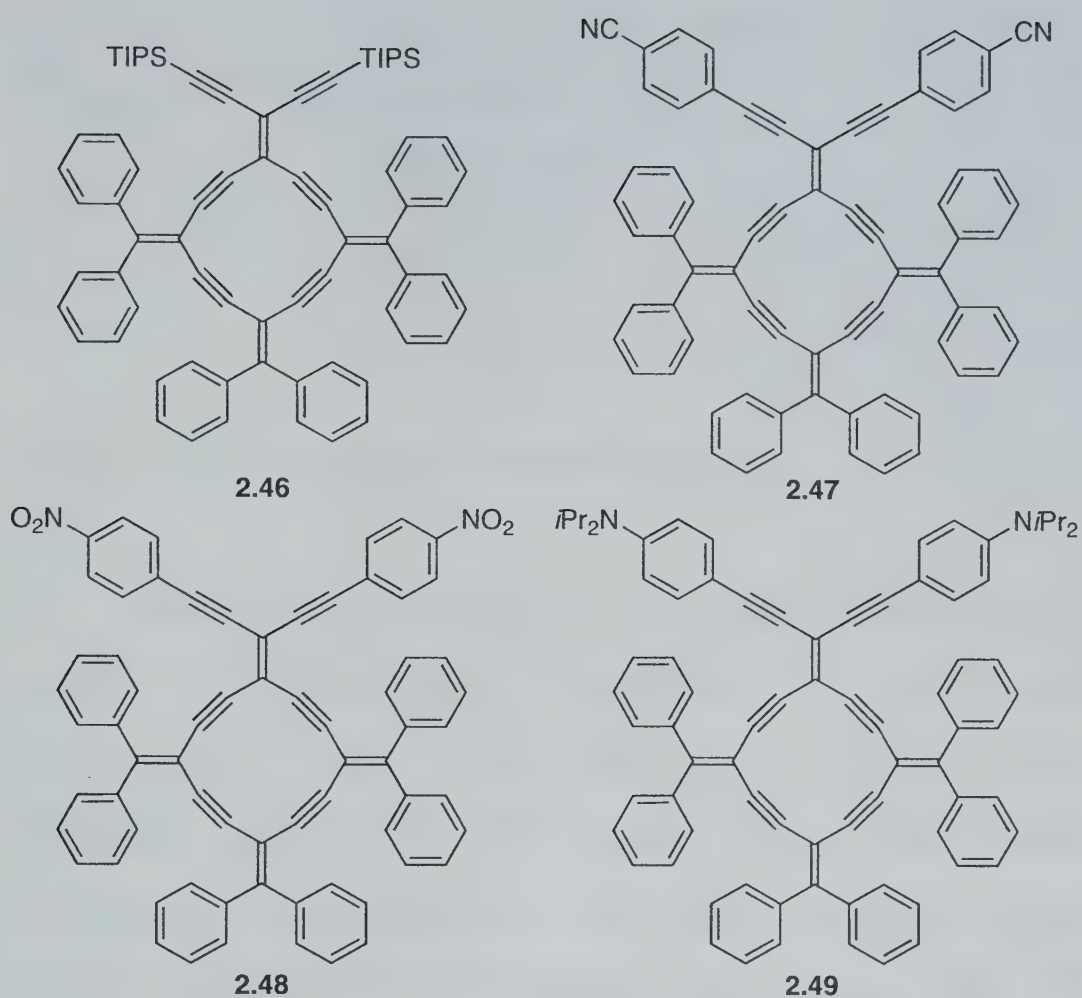
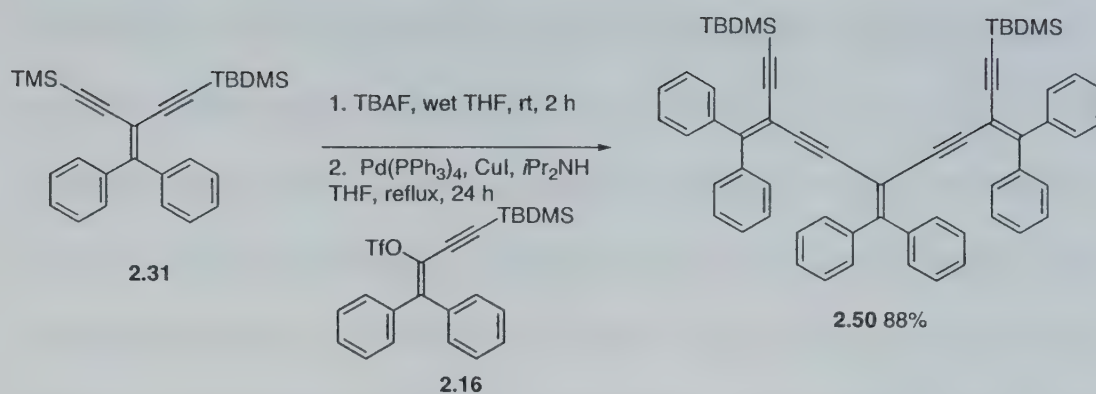


Figure 2-4 Series of [4]ERs based on model system **2.46**

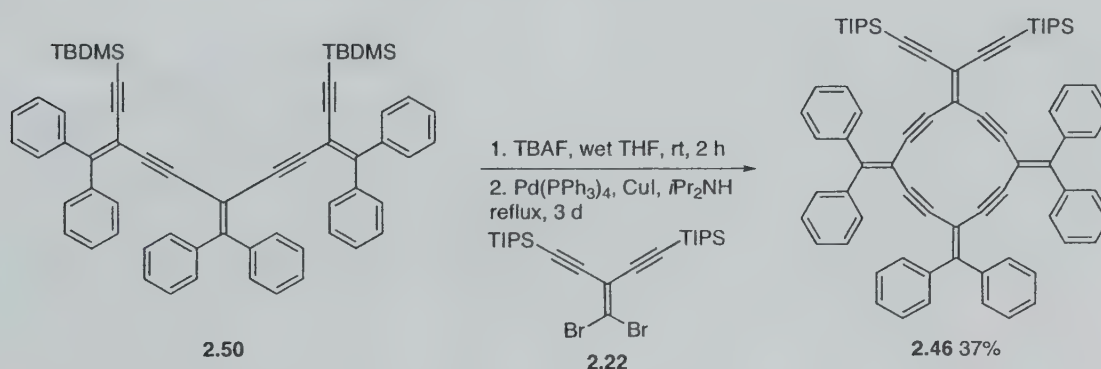
The assembly of the model compound **2.46** began with the synthesis of perphenylated *iso*-PDA **2.50**, which has been previously synthesized in our group (Scheme 2-17).^{4d,12} *iso*-PDA **2.50** was isolated after FCC in very good yield as a yellow foam.



Scheme 2-17 Synthesis of the perphenylated trimer **2.50**

Compound **2.46** (Scheme 2-18) was then synthesized as a progenitor of the other analogs in the model series.^{4d} The formation of this model **[4]ER** was not a trivial process and required significant optimization. Removal of the TBDMS groups in **2.50** with TBAF provided the perphenylated terminal diyne as a dark yellow oil after aqueous work-up and concentration. The desilylated *iso*-PDA and the TIPS-dibromoolefin **2.22** were then reacted in a sealed flask for three days under Sonogashira cross-coupling conditions to provide the desired **[4]ER** **2.46** in 6.3% yield after FCC. The poor yield of this reaction was attributed to dilute reaction conditions (ca. 0.005 M) since the isolated yield went from 6-9% to 13-16% upon increasing the concentration of the reaction (ca. 0.01 M). In an effort to further optimize the reaction, the temperature was increased to reflux and an almost three-fold increase of the isolated yield was observed. PdCl₂(PPh₃)₂ was also tried as a catalyst under otherwise identical conditions, but this led to the formation of a more complex mixture of products. Apart from the nature of the catalyst used, it

was still believed that adventitious oxygen was partially responsible for the less than stellar performance of this macrocyclization. TLC analysis of all reaction mixtures after radialene formation suggested the formation of numerous by-products from competing reactions, likely the result of inter- and intramolecular homocoupling reactions. The purification process also required optimization due to the presence of impurities with nearly identical polarity and solubility as product **2.46**. After significant trial and error, purification of the desired **[4]ER** was accomplished by first performing FCC (silica gel, CH₂Cl₂/hexanes 1:3) as the eluent and then recrystallizing the solid residue, obtained after removal of solvents, with CH₂Cl₂/hexanes at 5 °C to provide model **[4]ER 2.46** in high purity as a yellow powder.¹⁶

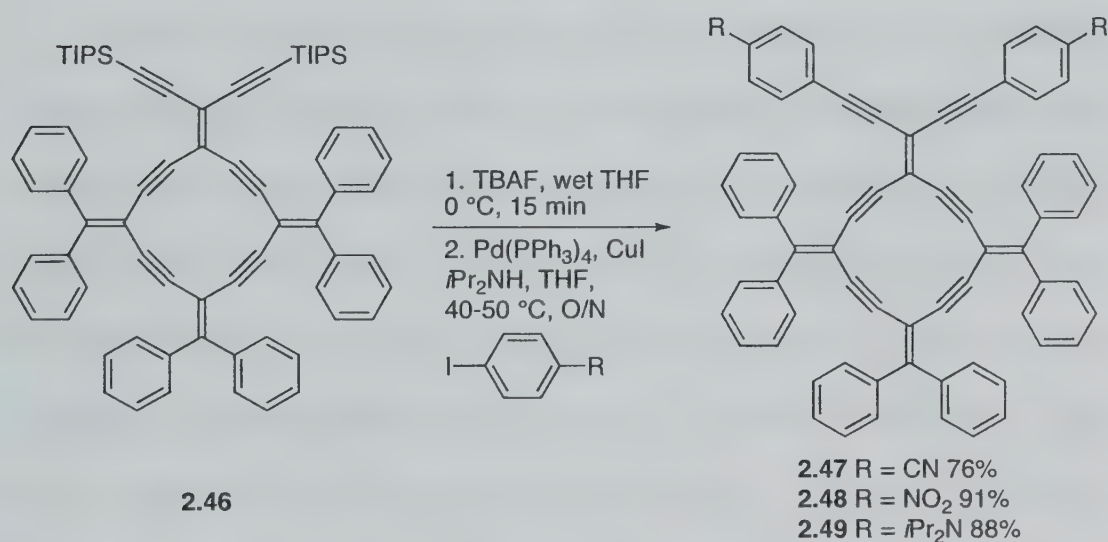


Scheme 2-18 Optimized synthesis of model **[4]ER 2.46**

With a reproducible method of synthesizing **2.46** in hand, the next task was to test whether desilylation would produce an intermediate suitable for further functionalization, as described in Scheme 2-19. The deprotection of **2.46** was effected by treatment with 2.2 equivalents of

TBAF for 15 minutes at 0 °C and proceeded without significant decomposition.

After the successful removal of the TIPS groups, attempts were made to introduce various aryl groups to the radialene core via Sonogashira cross-coupling (Scheme 2-19). Initially, this was accomplished using two equivalents of the desired aryl iodides under standard Sonogashira cross-coupling conditions at room temperature. The transformations were successful but reaction times were too long and isolation of the functionalized [4]ERs was tedious due to the presence of by-products with similar polarities. In an effort to improve this reaction, heat was applied. This led to a dramatic improvement of reaction times as well as the ease of purification of the [4]ERs.



Scheme 2-19 Synthesis of substituted-[4]ERs

The optimized procedure for the derivatization of the [4]ER is shown in Scheme 2-19. The purification process deserves some

comment. Following aqueous work-up, isolation of the **[4]ER** products was typically accomplished in two short steps. First, the crude reaction mixture was passed through a short plug of silica gel using varying ratios of EtOAc/hexanes (1:10 $\rightarrow$ 1:1). This process removed baseline material as well as the relatively nonpolar components. The filtrate was concentrated under reduced pressure, the solid residue was washed successively with hexanes and Et₂O, and the product dried under high vacuum to yield the **[4]ER**. It is noteworthy that **2.47** and **2.48** exhibited limited solubility, a property that was exploited in the purification process. On the other hand, the anilino analog **2.49** was more soluble in common organic solvents and typically required gradient FCC to provide samples of sufficient purity for characterization.¹⁶

With a modular approach for the introduction of electron-withdrawing and donating groups onto the periphery of model **[4]ER 2.46** now available, the next task was the synthesis of a **[4]ER** that would allow the incorporation of donors *and* acceptors in an analogous manner. In the intended series of molecules, the **[4]ER** framework would serve as an extended π -spacer between the donor and acceptor functionalities. With this in mind, two **[4]ERs** (**2.51** and **2.52**, Figure 2-5) were viewed as progenitors to donor and/or acceptor substituted **[4]ERs** and were synthesized concurrently.

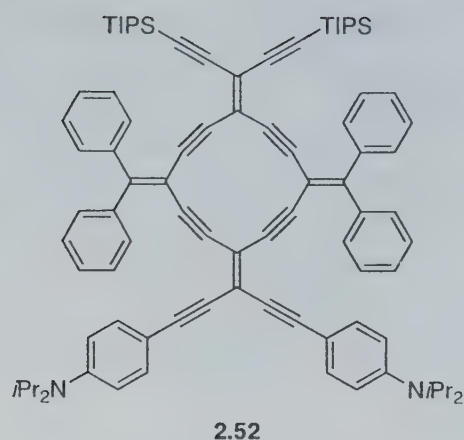
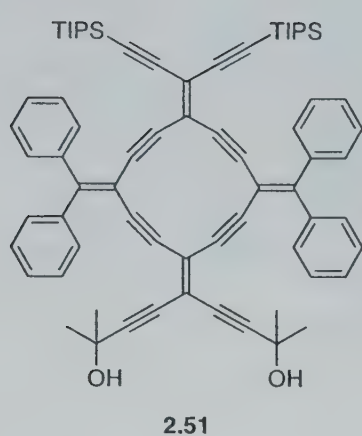
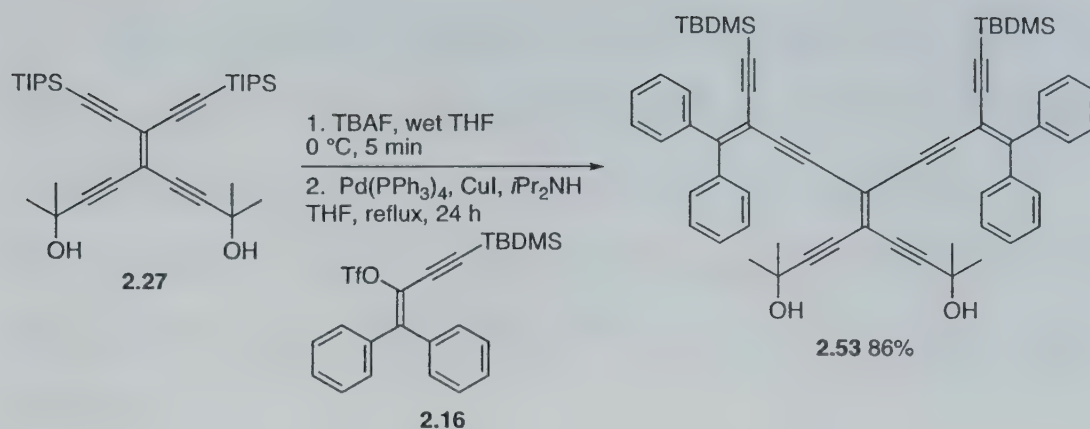


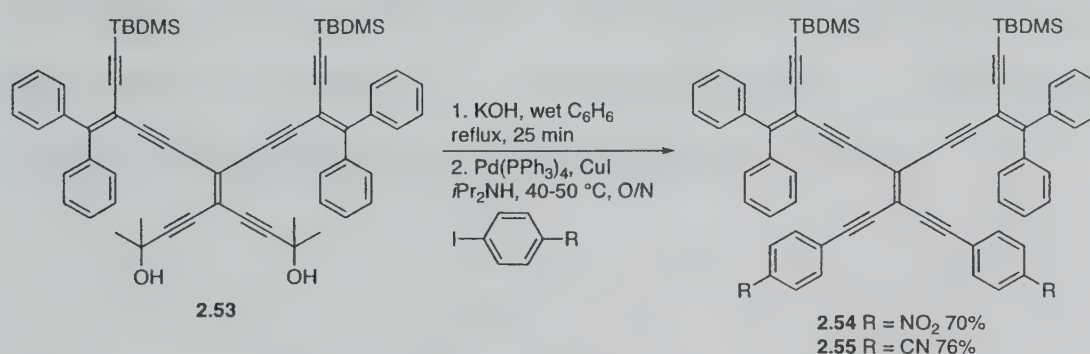
Figure 2-5 Precursors to D-A [4]ERs

It was envisioned that orthogonally protected [4]ER **2.51** would derive from *iso*-PDA **2.53** (Scheme 2-20). Selective removal of the TIPS groups in TEE **2.27** was accomplished using TBAF at 0 °C. Aqueous work-up and concentration under reduced pressure provided the terminal diyne, which was used in the next step without further purification. Sonogashira cross-coupling of the terminal diyne and the diphenyl vinyl triflate **2.16** afforded *iso*-PDA **2.53** following FCC (silica gel, EtOAc/hexanes 1:4) as a yellow foam in very good yield. The purification of *iso*-PDA **2.53** was aided substantially by the presence of the alcohol functionalities.



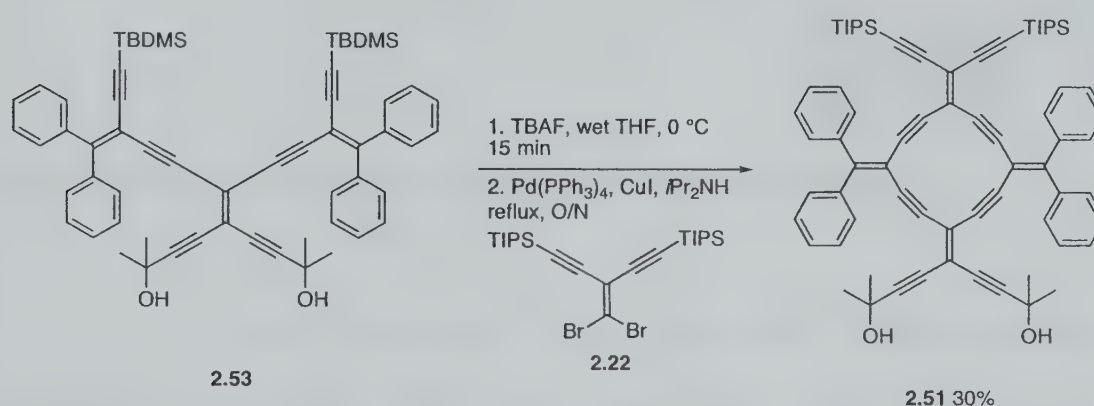
Scheme 2-20 Synthesis of an orthogonally protected *iso*-PDA **2.53**

The presence of orthogonal protecting groups in *iso*-PDA **2.53** made it a versatile building block that was used to synthesize nitrophenyl and benzonitrile analogs for a comparison of structure-property relationships. Using the method established by Diederich and co-workers,¹⁷ the acetonide groups in *iso*-PDA **2.53** were removed selectively using KOH in benzene at reflux. The terminal diyne was then subjected to Sonogashira cross-coupling with the desired aryl iodides to yield the desired *iso*-PDAs **2.54** and **2.55** in very good yield (Scheme 2-21).



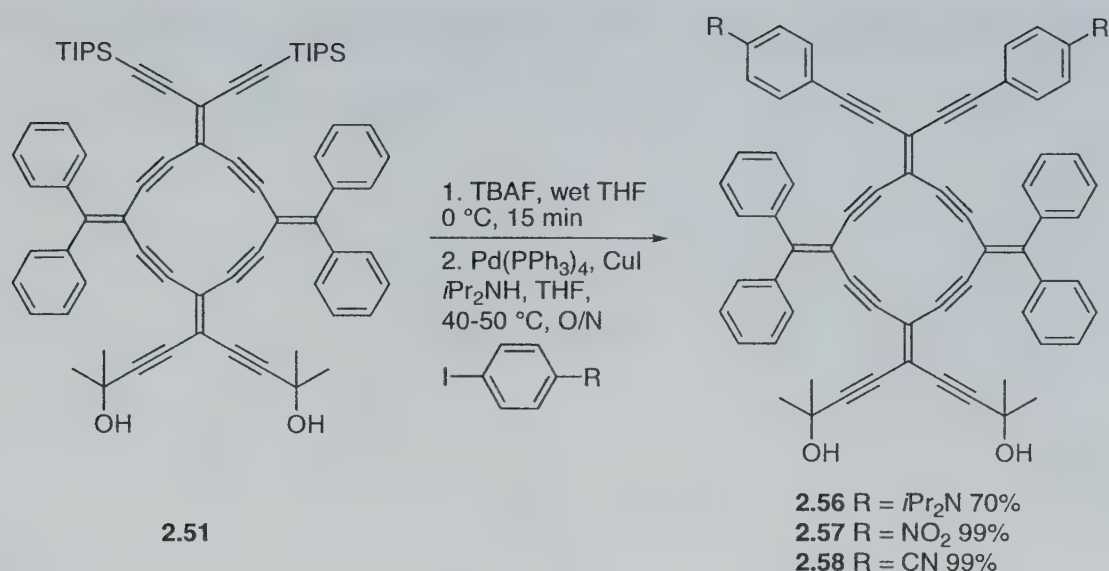
Scheme 2-21 Synthesis of *iso*-PDAs **2.54** and **2.55**

The synthesis of orthogonally protected **[4]ER 2.51** from the corresponding *iso*-PDA **2.53** is described in Scheme 2-22. The TBDMS groups in compound **2.53** were selectively removed using TBAF at 0 °C. The desilylated *iso*-PDA was then cross-coupled to the TIPS dibromoolefin **2.22** to afford **[4]ER 2.51** in reasonable yield as a yellow powder.¹⁶



Scheme 2-22 Formation of TIPS-acetonide **[4]ER, 2.51**

Derivatization of the orthogonally protected **[4]ER 2.51** was initially accomplished using the same protocol developed for **2.46** (Scheme 2-23). Desilylation of **2.51** using TBAF was followed by reaction with the appropriate aryl iodide in a Sonogashira reaction to produce the corresponding **[4]ERs** in good to excellent isolated yield.¹⁶

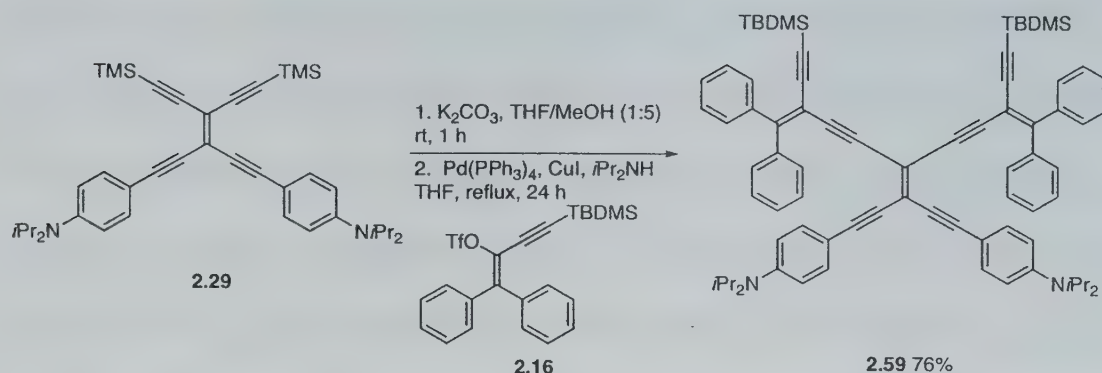


Scheme 2-23 Derivatization of the orthogonally protected **[4]ER 2.51**

A few notes on purification: the 4-ethynyl-*N*, *N*-diisopropylanilino functionalized derivative **2.56**¹⁶ was isolated as a black solid after FCC (silica gel, EtOAc/hexanes 1:5 → 3:5) as the eluent. Conversely, the acceptor-functionalized **[4]ERs 2.57**¹⁶ and **2.58**¹⁶ were purified as follows: The crude reaction mixtures were subjected to aqueous work-up and then concentrated under reduced pressure to give solids. The crude solids were then washed successively with hexanes (3 x 5 mL) and Et₂O (3 x 5 mL) to yield the **[4]ERs** as orange powders. Compounds **2.56-2.58** have not yet been deprotected and used as precursors to D-A substituted radialenes because of time constraints. The successful formation of **2.54** and **2.55**, however, suggest that this should be eminently possible.

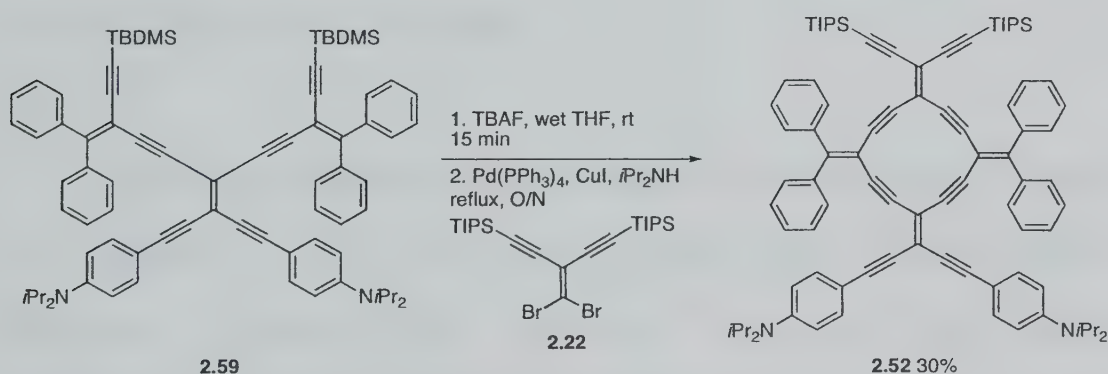
An alternative to D-A **[4]ER** formation was concurrently explored. The 4-*N,N*-diisopropylaniline substituted *iso*-PDA **2.59** was synthesized from **2.29** via desilylation and cross-coupling with triflate **2.16** (Scheme 2-

24). FCC (silica gel EtOAc/hexanes 1:40 → 1:20) provided *iso*-PDA **2.59** as a red foam in 76% yield.¹⁶



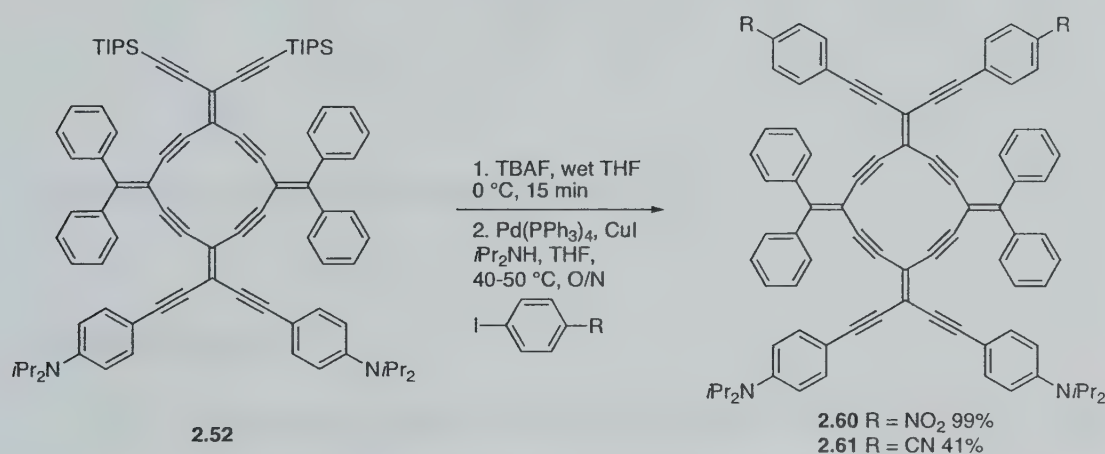
Scheme 2-24 Synthesis of *iso*-PDA **2.59**

Desilylation of *iso*-PDA **2.59** with TBAF was followed by Sonogashira cross-coupling of the terminal diyne with TIPS dibromoolefin **2.22**. As expected, this synthetic sequence afforded **[4]ER 2.52** (Scheme 2-25), which was isolated after FCC (silica gel, THF/hexanes 1:40 → 3:40) and recrystallization from CH_2Cl_2 /hexanes in reasonable yield as a red solid.¹⁶



Scheme 2-25 Synthesis of an anilino-substituted **[4]ER 2.52**

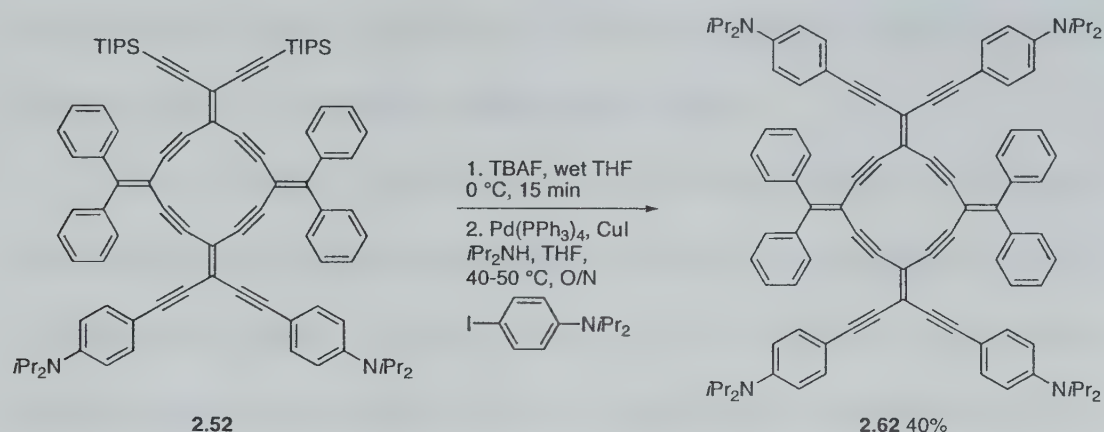
[4]ER 2.52 was subjected to desilylation conditions using TBAF and the resulting product used in cross-coupling reactions with aryl iodide partners. This produced the corresponding D-A substituted **[4]ERs** in reasonable to excellent isolated yield (Scheme 2-26).¹⁶ Much like the other nitrophenyl-functionalized **[4]ERs**, purification of **2.60** took advantage of its poor solubility in hexanes and Et₂O. On the other hand, FCC was used to provide the pure benzonitrile derivative **2.61** in 41% yield as a brown solid. The disparity in isolated yields was therefore attributed to the nature of the purification method.



Scheme 2-26 Synthesis of D-A **[4]ERs**

[4]ER 2.62 (Scheme 2-27) was targeted as an interesting molecule for comparison to **2.60** and **2.61**, particularly since donor-substituted expanded radialenes can demonstrate interesting and unique optoelectronic properties compared to their D-A counterparts.¹⁸ The symmetrical **[4]ER 2.62** was synthesized from **2.52** using the now general method in a modest yield of 40% as a red solid.¹⁶ Purification of **2.62**

displayed limited solubility in most common organic solvents. After a significant amount of trial and error attempts, however, the best technique was found to be a combination of silica gel filtration (MeOH/CH₂Cl₂ 3:100), removal of solvents, and washing of the solid residue with Et₂O to remove a very persistent impurity whose structure has remained unknown.



Scheme 2-27 Synthesis of symmetrical [4]ER **2.62**

2.4 Conclusions

The Sonogashira cross-coupling reaction between vinyl triflates **2.11** or **2.16** and various DEEs and TEEs was successfully used to generate *iso*-PDAs containing a broad range of functionalities including orthogonally-protected alkynes and electron-donating groups. A complementary approach that relied on the use of orthogonal protecting groups was also developed for the incorporation of electron-withdrawing functionalities as in compounds **2.54** and **2.55**.

Iso-PDAs derived from vinyl triflate **2.11** were not particularly good substrates for the subsequent macrocyclization reactions and did not

provide sufficient quantities of **[4]ERs** for characterization and structure-property relationship studies. On the other hand, three of the *iso*-PDAs derived from vinyl triflate **2.16** were converted successfully to the corresponding **[4]ERs** in satisfactory to excellent yields. Furthermore a viable route towards donor and/or acceptor substituted **[4]ERs** has been developed and used to synthesize the first examples of **[4]ERs** bearing strongly electron-donating and withdrawing groups.

The solubility characteristics of the highly functionalized **[4]ERs** were dependent on the appended groups. For example, **[4]ERs** containing *N,N*-diisopropylanilino groups exhibit good solubility and stability properties while those containing the strongly electron-withdrawing groups such as the nitrophenyl or benzonitrile groups are not particularly soluble and required more effort for dissolution. Cyclic voltammetry, NMR, UV-Vis and fluorescence spectroscopies have been used to establish structure-property relationships of within the various series of *iso*-PDAs and **[4]ERs** synthesized herein and these results will be discussed in Chapter 3.

2.5 References and notes

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Chapter 3 Structure-property relationships of donor- and/or acceptor-substituted cross-conjugated oligomers and macrocycles

3.1 Introduction

As described in the previous chapter, the Tykwinski group has contributed significantly to the development of modular approaches for the synthesis of *iso*-PDAs and **[*n*]ERs**.¹ For example, a generalized protocol has been used to gain access to **[*n*]ERs** with acetylene,^{1a,2} diacetylene^{1,3} heteroaromatic,^{3b-d} and transition metals^{3b-d,2c} used as the π -spacer in the cyclic framework. These **[*n*]ERs** typically display interesting structural, electronic, and optical properties.^{1b} For example, UV-Vis spectroscopic analysis of a series of perphenylated macrocycles shows that the electronic properties are contingent on the degree of strain in the structure.^{2b} In another example, hybrid **[*n*]ERs** bearing a pyridyl group demonstrate the ability to serve as self-assembling motifs in supramolecular chemistry.^{3b,e}

It has been a longstanding goal in the Tykwinski group to be able to: (1) exploit the 2D-conjugated framework of **[*n*]ERs** to gain access to novel push-pull systems, and (2) tune the electronic, optical, and nonlinear optical properties of the **[*n*]ERs** via incorporation of donors and/or acceptors. The ability to control the properties of **[*n*]ERs** at the molecular level can also have an impact on the overall properties of the bulk material, which might be useful for applications in third-order nonlinear

optics as well as molecular electronic devices.⁴ This chapter deals with characterization of molecules whose syntheses have been described in Chapter 2. Some of the characterization tools include ^1H - and ^{13}C NMR spectroscopies, differential scanning calorimetry (DSC) and melting point analyses, as well as HR MALDI or ESI mass spectrometry. The investigation of structure-property relationships in this thesis relies mainly on UV-Vis and fluorescence spectroscopies and cyclic voltammetry.

3.2 Cross-conjugated oligomers based on vinyl triflate 2.11

The first series of *iso*-PDAs (Figure 3-1) to be investigated are derived from the diisopropylanilino vinyl triflate **2.11**. They have been investigated for structure-property relationships with the aid of ^{13}C -NMR, UV-Vis and fluorescence spectroscopies.

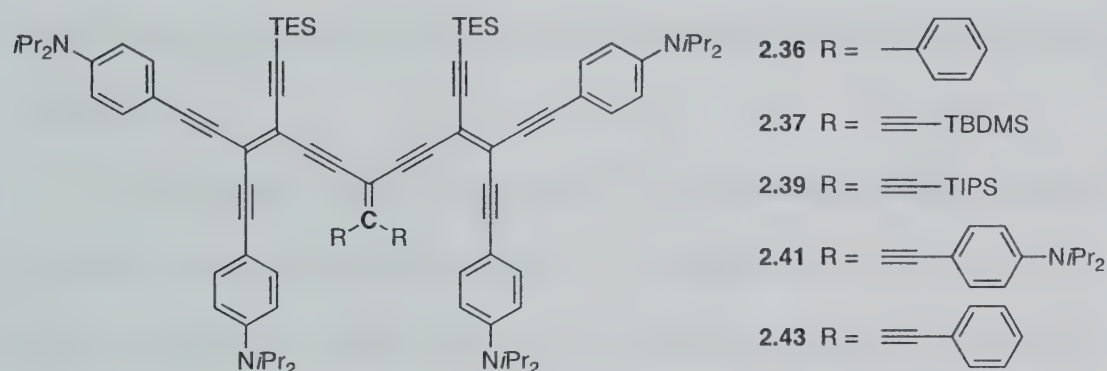


Figure 3-1 *iso*-PDAs based on **2.11**

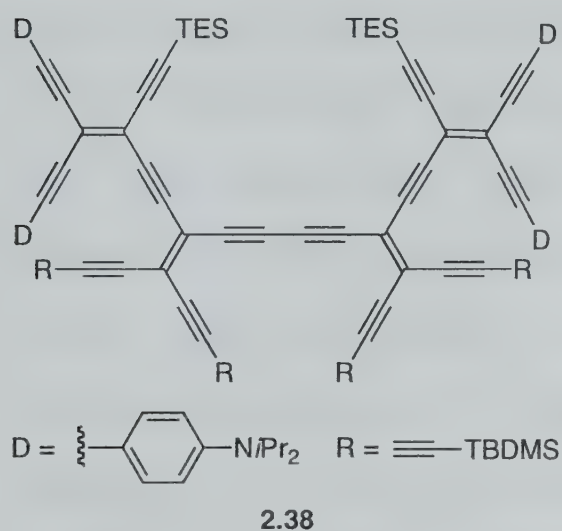
3.2.1 Physical characteristics

Iso-PDAs **2.36**, **2.37**, **2.39**, **2.41**, and **2.43** (Figure 3-1) exhibit reasonable thermal stability, and all show decomposition points above 125 °C. This has been confirmed via melting point determination and DSC measurements. The ^1H - and ^{13}C NMR spectroscopic data for the trimeric *iso*-PDAs are consistent with the proposed structures. Further evidence to allow unequivocal identification of the *iso*-PDAs is provided by HR mass spectrometry.

The ^{13}C NMR spectra of **2.36**, **2.37**, **2.39**, **2.41**, and **2.43** deserve a closer look. Providing that there is no significant chemical shift degeneracy, the ^{13}C NMR spectrum should show 30 unique resonances for the proposed symmetrical structure of model compound **2.36**. ^{13}C NMR spectroscopic analysis of model compound **2.36** reveals that there is indeed only one compound present and 30 unique carbon resonances are observed.

In the case of **2.37** and **2.39**, ^{13}C NMR spectroscopic analysis indicates the 30 resonances out of 31 expected (one sp^3 carbon not observed) and 29 signals out of 30 expected (one sp^2 carbon not observed), respectively. The chemical shifts of the carbons observed for **2.37** and **2.39** are quite similar, as expected, since they are structurally related. The ^{13}C NMR spectrum of *iso*-PDA **2.41** shows 32 resonances (out of 34 expected, one sp^3 and one sp^2 carbon not observed), which is expected because of the high degree of symmetry and presence of only

diisopropylanilino groups on the cross-conjugated backbone. The ^{13}C NMR spectroscopic analysis of *iso*-PDA **2.43** reveals 30 resonances corresponding to the 30 unique carbons in the proposed structure. Finally, in the case of byproduct, **2.38**, 36 resonances out of the 38 expected are seen, with one sp^3 and one sp^2 carbon not observed. The above discussion shows that it is typically the sp^3 and sp^2 carbons of the diisopropylanilino moieties that are degenerate and therefore sometimes not observed in the ^{13}C NMR spectra for this class of *iso*-PDA oligomers.



Considering specific NMR chemical shifts, only the vinylidene carbon outside the main chain ($\text{R}_2\text{C}=\text{C}$, see Fig 3-1) shifts dramatically upfield from ca. 157 ppm for **2.36** to ca. 120-122 ppm for all other members in this series. Aside from this, there is no significant change in the chemical shifts of the sp^2 - or sp -carbons of *iso*-PDAs **2.37-2.39**, **2.41** and **2.43**.

It is worthy to note that the chemical shift(s) of the quaternary aryl carbons in the aniline residues bound to nitrogen remain relatively

unchanged at ca. 149 ppm for each derivative. As expected on the basis of the inductively withdrawing nitrogen atom, these carbon atoms are the most downfield resonances in the ^{13}C NMR spectra throughout the series of *iso*-PDAs **2.37-2.39**, **2.41** and **2.43**.

3.2.2 Electronic absorption properties

The absorption spectra of *iso*-PDAs **2.36**, **2.37**, **2.39**, **2.41**, and **2.43** (Figure 3-2) have been measured in CH_2Cl_2 at room temperature and the results are summarized in Table 3-1. The UV-Vis spectrum of model compound **2.36** shows two major absorption maxima at 319 nm ($60\,800\text{ M}^{-1}\text{cm}^{-1}$) and 465 nm ($93\,900\text{ M}^{-1}\text{cm}^{-1}$) with evidence of a weak shoulder absorption at ca. 500 nm. As expected, **2.37** and **2.39** display very similar electronic absorption properties since they contain the same longest linearly conjugated segment. The formal exchange of the phenyl groups of **2.36** with TBDMS-ethynyl or TIPS-ethynyl groups as in **2.37** and **2.39**, respectively, does not have a significant effect on the most intense UV-Vis absorption, found at 471 ($70\,000\text{ M}^{-1}\text{cm}^{-1}$) and 468 nm ($62\,000\text{ M}^{-1}\text{cm}^{-1}$) for **2.37** and **2.39**, respectively. For both **2.37** and **2.39**, a shoulder absorption is now noticeable at ca. $\lambda_{\text{max}} = 547\text{ nm}$ ($35\,400\text{ M}^{-1}\text{cm}^{-1}$) and $\lambda_{\text{max}} = 538\text{ nm}$ ($35\,000\text{ M}^{-1}\text{cm}^{-1}$), respectively. The introduction of phenyl groups on the periphery of central TEE unit (i.e., **2.43**) results in a bathochromic shift of ca. 20 nm for the most intense absorption (488 nm, $\epsilon = 70\,000\text{ M}^{-1}\text{cm}^{-1}$) relative to that of **2.37** and **2.39**. As with **2.37** and **2.39**,

a significant shoulder absorption is also visible at lower energy, this time at ca. $\lambda_{\text{max}} = 560 \text{ nm}$ ($42\,500 \text{ M}^{-1}\text{cm}^{-1}$). Decoration of the central TEE unit with diisopropylaniline groups, as in **2.41**, results in the most dramatic spectral changes in the lower-energy UV-Vis region. While the most intense signal of **2.41** at 487 nm ($88\,000 \text{ M}^{-1}\text{cm}^{-1}$) is similar to that of **2.43**, a significant new band appears at 609 nm ($56\,100 \text{ M}^{-1}\text{cm}^{-1}$) for **2.41**.

Thus, there is overall little change in energy for the major absorption signal found between $465\text{--}488 \text{ nm}$ for *iso*-PDAs **2.36**, **2.37**, **2.39**, **2.41**, and **2.43** (Figure 3-2) upon decoration of the central TEE unit. The bathochromic shift of the lowest energy absorption for **2.36** (465 nm) vs. **2.43** (560 nm) may certainly be attributed to an extension of the longest linearly π -conjugated pathway in the latter molecule. The same can be said for the comparison of **2.37** (547 nm) and **2.39** (538 nm) in comparison to either **2.41** (609 nm) or **2.43** (560 nm). The origin of the strong lowest energy absorption of **2.41** has not yet been determined, but it may simply be an augmentation of the shoulder absorption observed in each **2.37**, **2.39**, and **2.43**. This shoulder, in turn, is reasonably attributed to an additional contribution from enhanced intramolecular charge-transfer interactions upon incorporation of the two additional alkyne units.⁴ The bathochromic shift of the shoulder absorption progressing from **2.39** to **2.43** to **2.41** is also suggestive of charge-transfer character. This conclusion is supported by the work of Diederich and coworkers who

made the same observations upon the introduction of increasingly strong aryl donor groups onto a series of TEE dimers.^{4c}

Finally, the molar absorptivities observed for this series of *iso*-PDAs show only a slight dependence based on the nature of the appended groups on the central DEE or TEE unit. It is nonetheless interesting to note the marginally larger molar absorptivity of phenyl substituted **2.36** in comparison to the others, even though the origin of this enhancement is not yet understood.

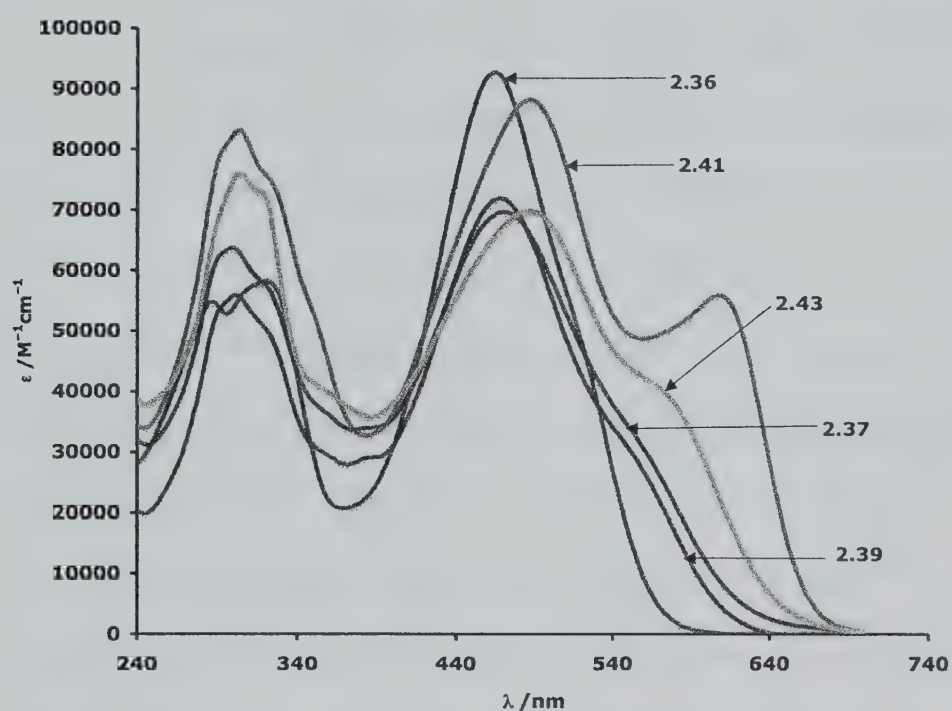


Figure 3-2 UV-Vis spectra of *iso*-PDAs **2.36**, **2.37**, **2.39**, **2.41**, and **2.43** in CH₂Cl₂

Table 3-1 Summary of the absorption maxima and molar extinction coefficients in the UV-Vis spectra of donor-substituted *iso*-PDAs in CH₂Cl₂

Compound	λ_{max} /nm ($\epsilon = [\text{M}^{-1}\text{cm}^{-1}]$)		
2.36	465 (93 900)	319 (60 800)	288 (54 800)
2.37	547 (sh, 35 400)	471 (70 000)	300 (64 000)
2.39	538 (sh, 35 000)	468 (72 000)	302 (56 000)
2.41	609 (56 100)	487 (88 000)	303 (83 000)
2.43	560 (sh, 42 500)	488 (70 000)	305 (76 000)
2.59	475 (44 300)	388 (23 600)	318 (50 300)

A comparison of the electronic absorption data of *iso*-PDA **2.41** to that of the TEE trimer **1.48** reported by Diederich and coworkers^{4e} (Figure 3-3) reveals that the energies of the major absorptions are almost identical at 487 (88 000 M⁻¹cm⁻¹) and 486 nm ($\epsilon = 98\,800\text{ M}^{-1}\text{cm}^{-1}$),^{4e} respectively. The spectrum of **1.48** also shows a shoulder at ca. 550 nm, although the authors did not comment on this. The lowest energy absorption observed for **1.48** was attributed to intramolecular charge-transfer from the dialkylanilino moieties to the electron-deficient TEE core.^{4a,e} The higher energy absorption for **1.48** and **2.41** are also quite similar occurring at 301 nm (96 700 M⁻¹cm⁻¹) and 303 nm (83 000 M⁻¹cm⁻¹). It is worthy to note that TEE trimers **1.48** and **2.41** bear the same number of anilino groups but differ in the arrangement of the central TEE moiety as well as the length of longest linearly conjugated pathway (shown in bold, Figure 3-3) and this may be responsible for any differences observed in the UV-Vis spectra of **1.48** and **2.41**.

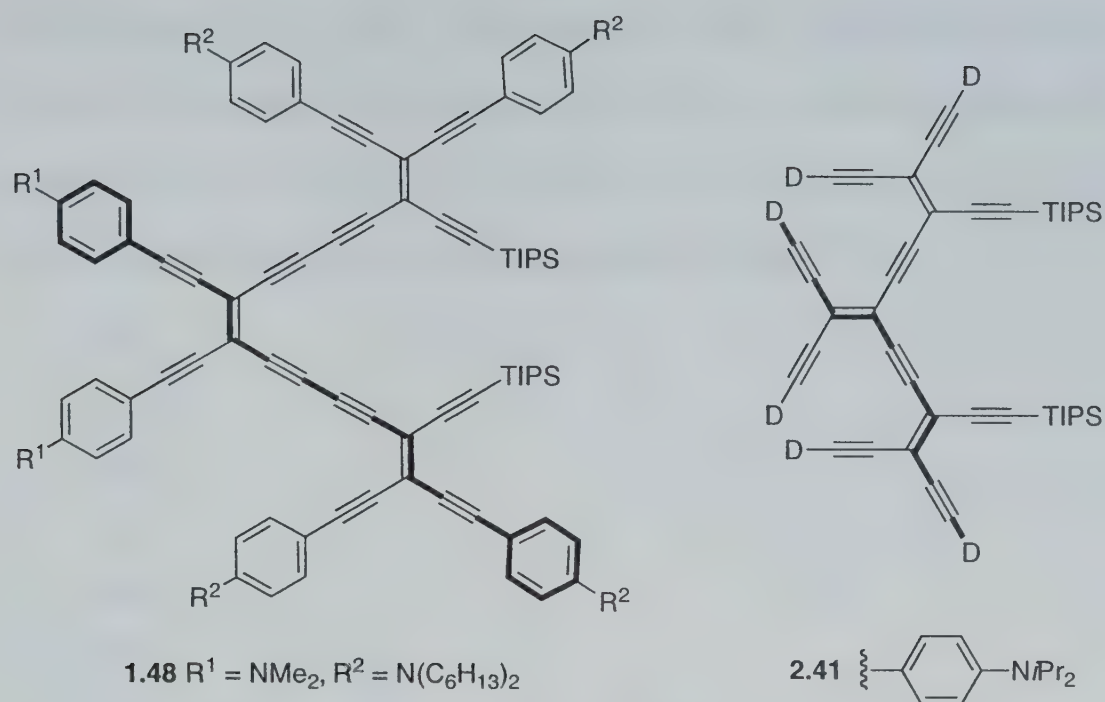


Figure 3-3 TEE trimers **1.48** and *iso*-PDA **2.41**

A comparison of the UV-Vis spectrum of **2.36** to that of **2.59** is also instructive, since they both contain exactly the same longest linearly conjugated π -electron segment (Figure 3-4, shown in bold). The λ_{max} value of **2.59** (475 nm) is red shifted by only 10 nm as compared to **2.36** (465 nm), while there is very little to no change in the UV region. In both spectra, however, there is evidence of a shoulder signal at lower energy (ca. 500 nm) relative to λ_{max} , although in neither case is this absorption well resolved. These observations suggest that there is minimal contribution from cross-conjugation, since λ_{max} of **2.36** and **2.59** remain essentially the same. There is, at present, no specific explanation for the significantly higher molar absorptivity of λ_{max} for **2.36** ($\epsilon = 93\,900\text{ M}^{-1}\text{cm}^{-1}$) relative to that of **2.59** ($\epsilon = 44\,300\text{ M}^{-1}\text{cm}^{-1}$) without the aid of

computational data. Likely, however, the number of strongly electron-donating dialkylanilino groups play a key role in the electronic absorption properties of these molecules, as has been observed previously by, for example, Diederich and coworkers on similar systems.^{4d}

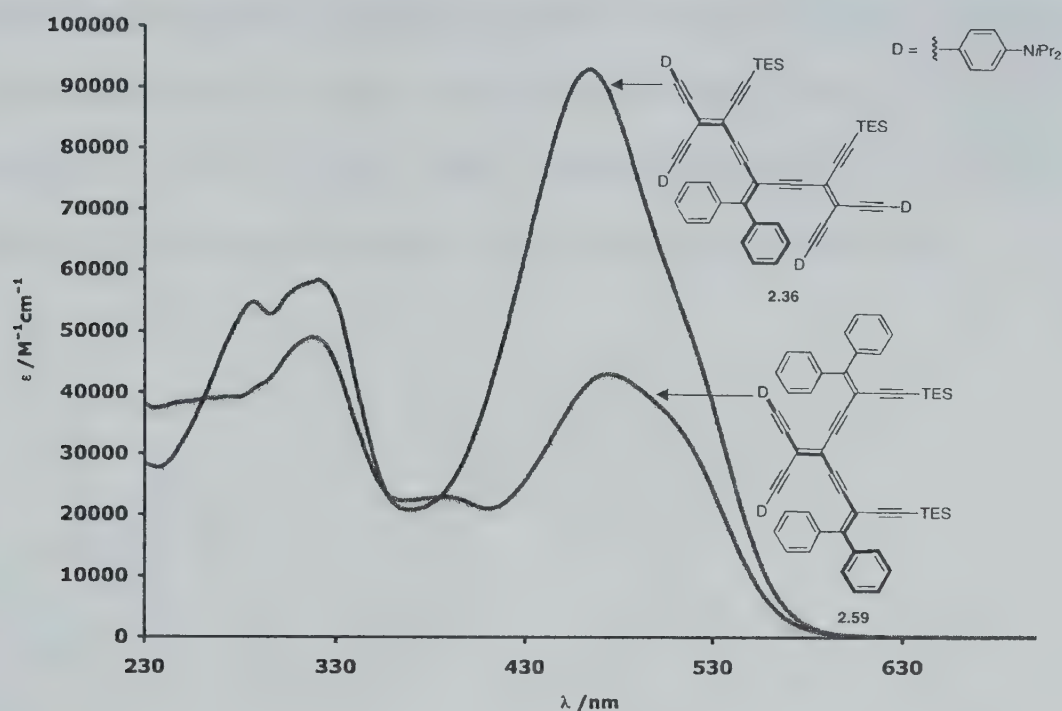


Figure 3-4 UV-vis spectra of *iso*-PDAs **2.36** and **2.59** in CH₂Cl₂

A comparison of the UV-Vis spectra of **2.37** and **2.38** (Figure 3-5) is interesting given that they contain identical linearly conjugated pathways that incorporate the anilino donors. They are dissimilar, however, in that **2.38** has a longer linearly conjugated enyne segment between the two internal TEE moieties (in bold, Fig 3-5). Provided that there is minimal contribution from cross-conjugation, the λ_{max} values for **2.37** and **2.38** might be expected to be similar. The spectra of **2.37** and **2.38** share the

common feature of two major absorption maxima. Both major absorption maxima of **2.37** are red-shifted by only ca. 20 nm in comparison to the λ_{max} of **2.38**. This may be attributed to the fact that cross-conjugation is inefficient and that the extent of π -electron delocalization is mainly limited to the longest-linearly conjugated segment in these *iso*-PDAs.^{4c} Two lower energy shoulders are also observed in the visible region of the UV-Vis spectrum of **2.38**. Without suitable model compounds for comparison, however, it is difficult to project as to the origin of these shoulders.

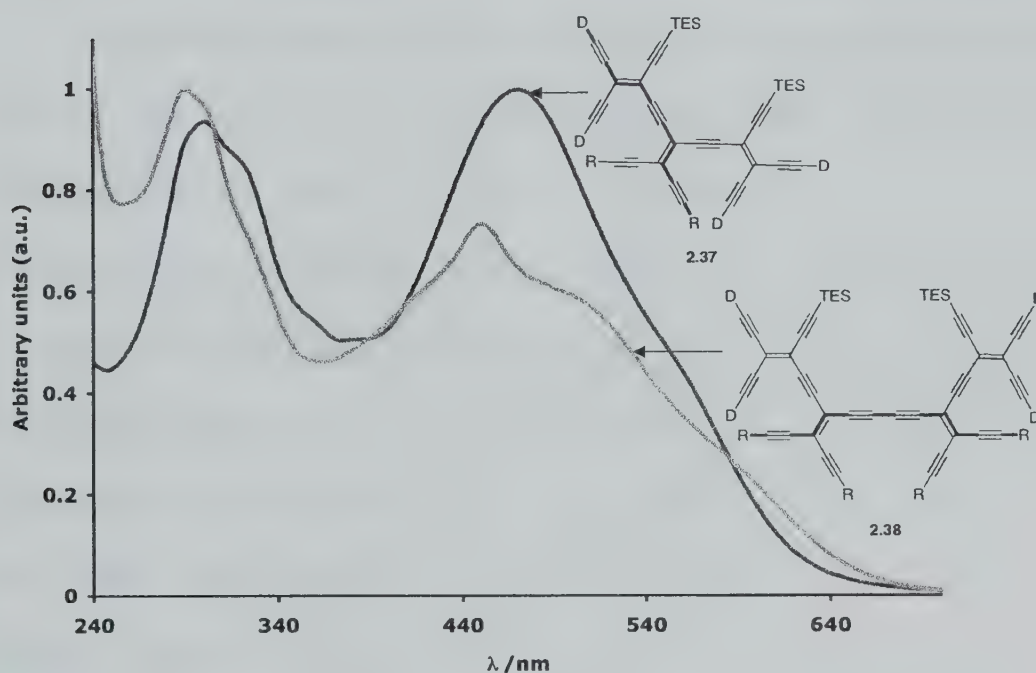


Figure 3-5 UV-Vis spectra of **2.37** and **2.38** in CH_2Cl_2

3.2.3 Emission properties of selected *iso*-PDAs

The fluorescence spectra of compounds **2.36**, **2.39**, **2.41** and **2.43** have been measured in CH₂Cl₂ at room temperature with an excitation wavelength (λ_{exc}) of 485 nm.⁵ The results are summarized in Figure 3-6 and Table 3-2. The *iso*-PDAs show a single broad emission peak (λ_{em}) whose intensity varies with the substituents on the central TEE unit. The relative intensities of **2.39** and **2.41** are essentially the same and the lowest observed in the series. Model compound **2.36** has the highest relative intensity and largest observed Stokes shift (166 nm) while **2.41** has the second highest relative intensity and the smallest observed Stokes shift (64 nm). The smaller observed Stokes shift of **2.41** as compared to the other members of this series of *iso*-PDAs may be attributed to the fact that the additional aniline residues serve to rigidify the molecule in the ground state through electron donation to the formally electron deficient enyne core. The observed Stokes shifts of **2.39** and **2.43** are similar (136 and 139 nm, respectively) and fall between those of **2.36** and **2.41**. The maximum emission wavelength (λ_{em}) shifts to lower energies upon introduction of triisopropylsilyl substituents and aryl donors onto the central TEE unit. The emission wavelength does not vary as a function of excitation wavelength (λ_{exc} = 295 or 485 nm), suggesting that emission occurs from similar excited states for **2.36**. This statement is also true for **2.39**, **2.41**, and **2.43**.

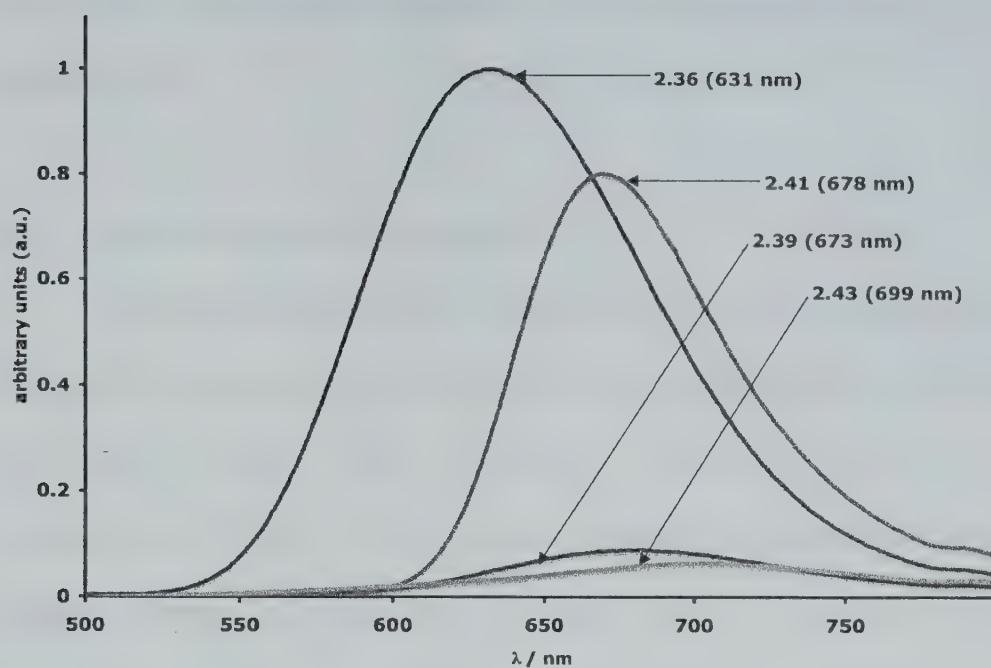


Figure 3-6 Selected emission spectra of **2.36**, **2.39**, **2.41**, and **2.43** in CH_2Cl_2 ; λ_{em} [nm] for each *iso*-PDA is shown in parentheses ($\lambda_{\text{exc}} = 485 \text{ nm}$)

Table 3-2 Qualitative fluorescence data of **2.36**, **2.39**, **2.41**, and **2.43** in CH_2Cl_2 ^a

Compound	$\lambda_{\text{in}} / \text{nm}^b$	$\lambda_{\text{max}} / \text{nm}^c$	$\lambda_{\text{em}} / \text{nm}$	Stokes Shift / nm
2.36	465	465	631	166
2.39	468	538	674	136
2.41	487	609	673	64
2.43	488	560	699	139

^a $\lambda_{\text{exc}} = 485 \text{ nm}$ ^b Wavelength of most intense absorption beyond 400 nm.

^c Lowest-energy absorption maxima.

3.3 Cross-conjugated oligomers and macrocycles based on vinyl triflate 2.16

3.3.1 Cross-conjugated oligomers

The second series of *iso*-PDAs **2.50**, **2.53–2.55** and **2.59** (Figure 3-7) has been investigated for structure-property relationships with the aid of ^{13}C NMR, UV-Vis and fluorescence spectroscopies, and cyclic voltammetry. It was envisioned that apart from establishing structure-property relationships within the series, they can also be used for comparison of properties to those of the corresponding **[4]ERs** to gain a better understanding of the properties of the latter resulting from macrocyclization.

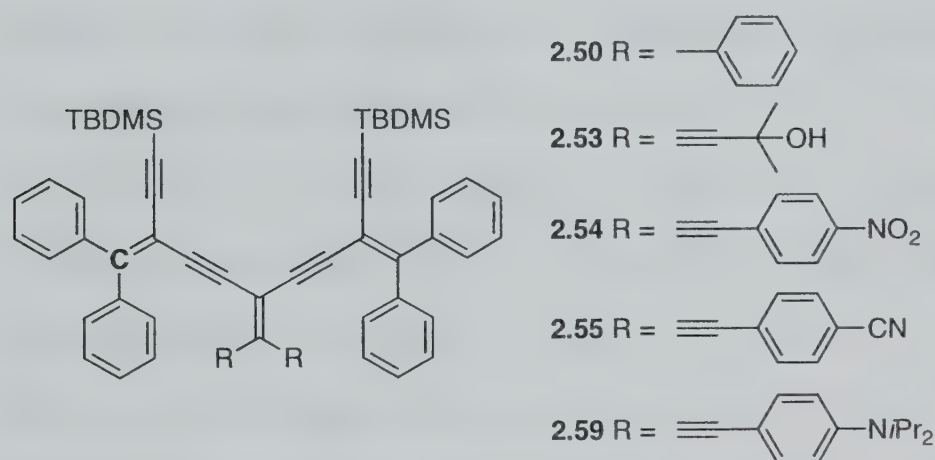


Figure 3-7 *iso*-PDAs based on **2.16**

3.3.1.1 Physical characteristics

The *iso*-PDAs derived from diphenyl vinyl triflate **2.16** (Figure 3-7) demonstrate reasonable thermal stability. Compound **2.50** has a melting point above $>180\text{ }^{\circ}\text{C}$, which is consistent with that previously reported.⁶ While **2.53** has a relatively low melting point below $70\text{ }^{\circ}\text{C}$, *iso*-PDAs **2.54** and **2.59** both have melting points of ca. $160\text{ }^{\circ}\text{C}$ as confirmed by DSC. *Iso*-PDA **2.55**, on the other hand, shows only a decomposition point, at ca. $110\text{ }^{\circ}\text{C}$. The ^{13}C and ^1H NMR spectroscopic data of **2.50** are consistent with that reported,⁶ and that of **2.53–2.55** and **2.59** are consistent with the proposed structures. Additional evidence to support the structures is provided by HR mass spectrometry.

A comparison of the ^{13}C NMR spectra of **2.50**, **2.53–2.55**, and **2.59** reveals no significant changes in the chemical shift of key carbon atoms as a function of substitution about the central TEE core. For example, the most diagnostic carbon in *iso*-PDAs is typically the vinylidene carbon outside the main chain ($\text{Ph}_2\text{C}=\text{C}$, see Figure 3-7, bolded carbon atom).⁶ This carbon shifts downfield from 156.7 ppm for **2.50** to 158.6 ppm for **2.53** and from 160 ppm for **2.54** (or **2.55**) to 158 ppm for **2.59**. Of note is the fact that there is no chemical shift degeneracy observed for the carbon atoms of the *iso*-PDAs in this series; ^{13}C NMR spectrum of **2.53** shows all 23 unique signals, while those of **2.54**, **2.55**, and **2.59** show 25, 26, and 27 resonances, respectively.

3.3.1.2 Electronic absorption properties

The electronic absorption behavior of *iso*-PDAs **2.50**, **2.53–2.55**, and **2.59** has been investigated by UV-Vis spectroscopy as measured in CH₂Cl₂ at room temperature. The results are summarized in Figure 3-8 and Table 3-3. The lowest energy absorption maximum of **2.50**⁶ and **2.53** are centered at energies of $\lambda_{\text{max}} = 361 \text{ nm}$ ($31\,600 \text{ M}^{-1}\text{cm}^{-1}$) and of $\lambda_{\text{max}} = 395 \text{ nm}$ ($28\,500 \text{ M}^{-1}\text{cm}^{-1}$), respectively. A bathochromic shift (34 nm) is observed on going from **2.50** to **2.53** and this may be attributed to an extension of the overall π -conjugation chromophore. The lowest energy λ_{max} of **2.54**, **2.55**, and **2.59** is bathochromically shifted by 65, 53, and, 80 nm, respectively, as compared to **2.53**. As mentioned earlier in this chapter, a weak shoulder absorption is noticeable at ca. 500 nm in the spectrum of **2.59** (see **Figure 3-5**), while this shoulder appears to be absent from the spectra of **2.54** and **2.55**. The much larger shift observed for **2.59** relative to **2.54** and **2.55** could be the result of additional contribution from intramolecular charge-transfer interactions between the diisopropylaniline groups and the electron-accepting TEE core of **2.59**.⁴ Support for this premise comes from similar investigations of the electronic absorption characteristics by Diederich and coworkers on similar systems.^{4b,c} The authors report that there are large bathochromic shifts in λ_{max} upon going from TIPS substituents to dialkylanilino substituents on the cross-conjugated backbone of a series of TEE dimers.^{4c}

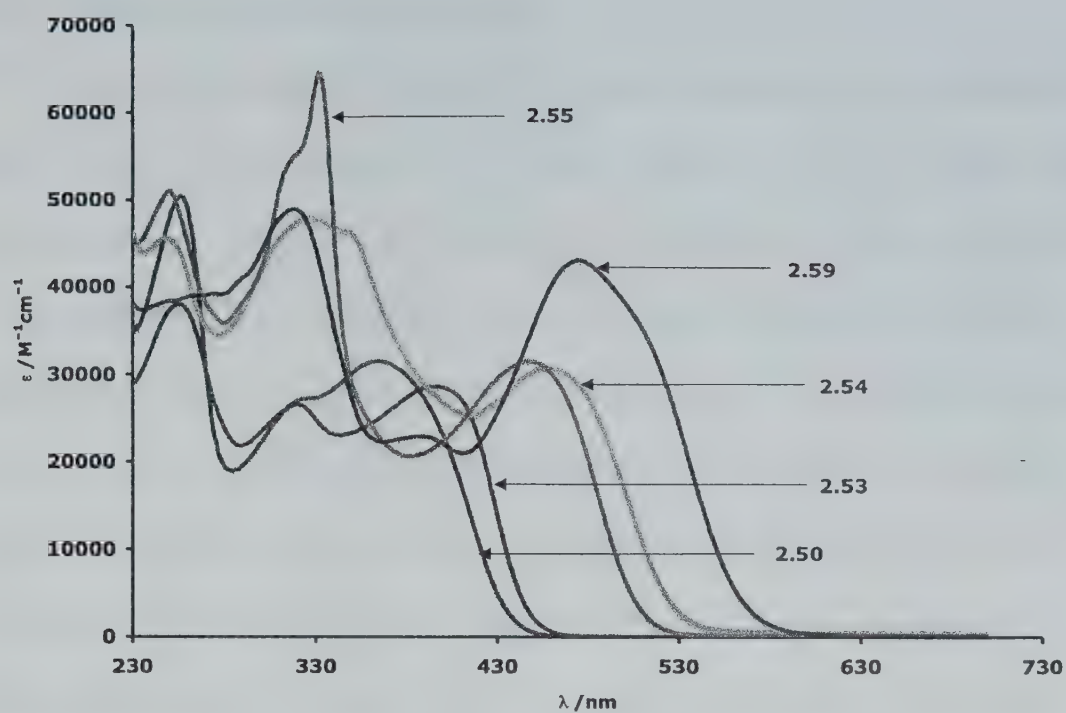


Figure 3-8 UV-Vis spectra of **2.50**, **2.53-2.55**, and **2.59** in CH_2Cl_2

Table 3-3 Absorption maxima and molar absorptivities of **2.50**, **2.53-2.55**, and **2.59** in CH_2Cl_2

Compound	$\lambda_{\text{max}} / \text{nm}$ ($\epsilon = [\text{M}^{-1} \text{cm}^{-1}]$)		
2.50	361 (31 600)	325 (27 300)	256 (50 500)
2.53	395 (28 500)	319 (26 600)	255 (38 100)
2.54	460 (30 700)	321 (47 600)	249 (45 600)
2.55	448 (31 600)	332 (64 700)	251 (51 100)
2.59	475 (44 300)	388 (23 600)	318 (50 300)

3.3.1.3 Electrochemical properties

Cyclic voltammetry experiments were conducted in collaboration with fellow group member Mr. Adrian Murray and the results are summarized in Table 3-4. As expected, the redox potentials of *iso*-PDAs **2.50**, and **2.53-2.55** and **2.59** (Table 3-4) show a strong dependence on the nature of the substituents on the TEE core. The *iso*-PDAs display either quasi-reversible (**2.50** and **2.53–2.55**) or irreversible (**2.59**) oxidation steps. Reversible reduction steps are observed only for **2.55**, while all other members of this series give quasi-reversible waves. The presence of the nitrophenyl or benzonitrile groups causes the first reduction potential of **2.54** and **2.55** to be shifted anodically as compared to **2.53**. Conversely, the presence of diisopropylaniline groups results in a dramatic decrease of the first oxidation potential from 1.07 V for **2.53** to 0.33 V for **2.59** consistent with the work of Diederich and coworkers on similar systems.^{4,7} It is worthy to note that the first reduction potential of **2.54** (–1.39 V) also agrees reasonably well with that observed for the corresponding TEE **A** (–1.38 V) while the second oxidation potential of **2.59** (0.47 V) agrees with that of TEE the corresponding **B** (0.42 V).^{7b} The electrochemical HOMO-LUMO gap decreases on going from **2.50** (3.01 eV) to **2.53** (2.87 eV). Similarly, a lowering of the electrochemical HOMO-LUMO gap is observed upon introduction of electron-withdrawing (**2.54**, 2.10 eV and **2.55**, 2.55 eV) and electron-donating groups (**2.59**, 2.10 eV). It is interesting to note

that the electrochemical HOMO-LUMO gap of **2.54** and **2.59** are similar despite the lower energy absorption found in the UV-Vis spectrum of **2.59**.

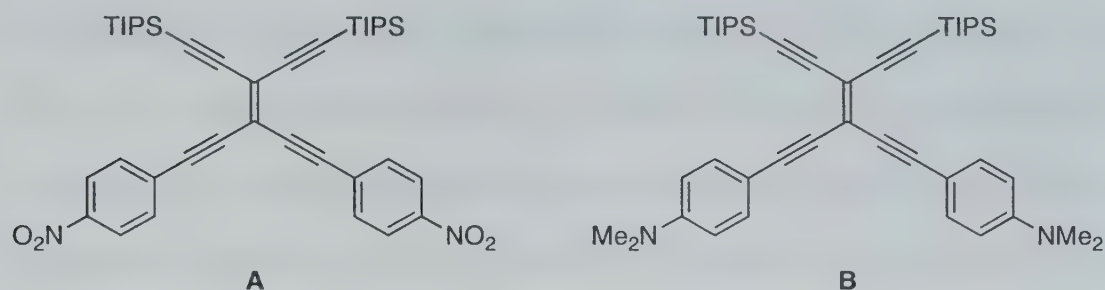


Table 3-4 Cyclic voltammetry data for *iso*-PDAs **2.50**, **2.53-2.55**, and **2.59**^a

Compound	E_{red1} <i>V</i>	E_{red2} <i>V</i>	E_{ox1} <i>V</i>	E_{ox2} <i>V</i>	E_{ox3} <i>V</i>	E_{ox4} <i>V</i>	$E_{\text{g}}^{\text{electro}}$ <i>eV</i> ^c
2.50	-2.09	-2.40	0.93	—	—	—	3.01
2.53	-1.81	-2.24	1.07	—	—	—	2.87
2.54	-1.39	-1.83	0.71	—	—	—	2.10
2.55	-1.49	-1.77	1.06	—	—	—	2.55
2.59	-1.79	-2.33	0.33 ^b	0.47 ^b	0.77 ^b	1.30 ^b	2.13

^a In deoxygenated CH_2Cl_2 on a Pt working electrode with a Ag/Ag^+ pseudoreference (0.01 M AgNO_3 , 0.1 M Bu_4NPF_6 in CH_3CN), and a Pt coil as counter electrode; Fc^+/Fc reference. ^b Peak potential, E° , for irreversible waves are estimated as $E^\circ = (E_{\text{peak}} + E_{\text{onset}})/2$. ^c Electrochemical HOMO-LUMO gap, $(E_{\text{ox1}} - E_{\text{red1}})$.

3.3.1.4 Emission properties

Emission spectra have been measured for **2.53–2.55** and **2.59** in deoxygenated CH_2Cl_2 with an excitation wavelength of 425 nm (Figure 3-9) and the results are summarized in Table 3-5. Each iso-PDA shows a single broad emission peak whose relative intensity varies as a function of substitution about the TEE core. Iso-PDA **2.53** shows the lowest intensity and the introduction of electron-donating and electron-withdrawing substituents in **2.53** leads to an increase in relative intensities in the following order: **2.55** < **2.54** < **2.59**. The maximum emission wavelength (λ_{em}) shifts toward lower-energy on going from **2.53** (λ_{em} = 487 nm) to **2.59** (λ_{em} = 609 nm). The observed Stokes shift **2.53–2.55** and **2.59** are 92 nm, 90 nm, 134 nm and, 106 nm respectively. There is currently no good explanation for the smaller Stokes shift values observed in the case of **2.53** and **2.55** without further studies such as theoretical calculations and X-ray crystallography. The emission wavelength does not vary as function of excitation wavelength (λ_{exc} = 364, 385, or 400 nm) suggesting that emission occurs from similar excited states for compound **2.53**. This statement is also true for compounds **2.54**, **2.55**, and **2.59**.

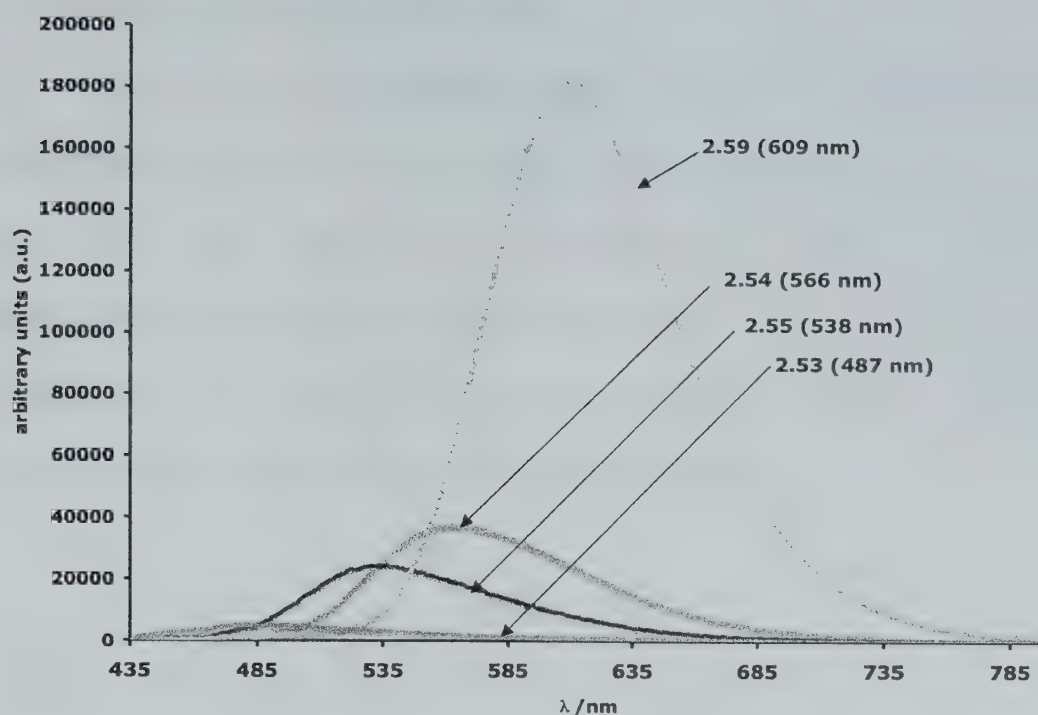


Figure 3-9 Emission spectra of **2.53-2.55** and **2.59**; λ_{em} [nm] for each *iso*-PDA is shown in parentheses

Table 3-5 Summary of qualitative fluorescence data of **2.53**, **2.54**, **2.55**, and **2.59** in CH_2Cl_2 ^a

Compound	λ_{max} /nm	λ_{em} /nm	Stokes Shift /nm
2.53	395	487	92
2.54	460	566	106
2.55	448	538	90
2.59	475	609	134

^a $\lambda_{exc} = 425$ nm

3.3.2 [4]ERs based on *iso*-PDA 2.50

The first series of [4]ERs to be examined for structure-property relationships contained either a donor or an acceptor (Figure 3-10). This was done using mainly cyclic voltammetry, ^{13}C NMR, UV-Vis and fluorescence spectroscopy. These radialenes also serve as model compounds to compare with other analogs to probe the electronic communication in the [4]ER π -conjugated framework.

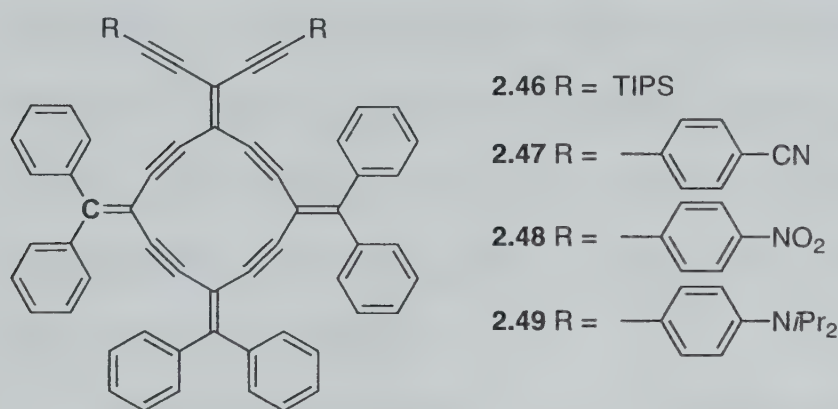


Figure 3-10 [4]ERs 2.46-2.49

3.3.2.1 Physical properties

[4]ERs 2.46-2.49 (Figure 3-10) are solids that exhibit thermal stability beyond 270 °C based on melting point determination and DSC analysis. HR mass spectrometric, ^1H - and ^{13}C NMR spectroscopic data for this series of [4]ERs are consistent with the structures proposed. In the ^{13}C NMR spectra, a consistent shift of the vinylidene carbon (shown in bold in Figure 3-10) is observed upon cyclization. It shifts upfield from 160 ppm (**2.55**) to 154.0 or 153.1 ppm (**2.47**), 160 ppm (**2.54**) to 154.2 or 153.2 ppm (**2.48**) and 158 ppm (**2.59**) to ca. 152 ppm (**2.49**). Additionally, the ^{13}C

NMR spectroscopic analysis of **2.46-2.49** shows no evidence of chemical shift degeneracy. The ^{13}C NMR spectra show 26, 29, 28 and 30 resonances for **2.46-2.49**, respectively.

3.3.2.2 Electronic absorption properties

It might be predicted that the electronic absorption properties of **[4]ERs 2.46-2.49** would mirror those of *iso*-PDAs **2.50**, **2.53**, **2.54**, **2.55**, and **2.59** due to the fact that they contain the identical longest linearly conjugated segment, including the pendent phenyl rings. A comparison of the two types of systems will provide information such as the effect of macrocyclization and the role of cross-conjugation, if any, in π -electron delocalization in the **[4]ERs**.

The electronic absorption spectra of **[4]ERs 2.46-2.49** have been measured in CH_2Cl_2 at room temperature and the results are summarized in Figure 3-11 and Table 3-6. The spectra of **2.46-2.48** share the common feature of a major absorption at ca. $\lambda_{\text{max}} = 400$ nm. A shoulder absorption of much weaker intensity is visible at ca. 430, 498 and 497 nm for **2.46-2.48**, respectively. The introduction of dialkylanilino groups into the periphery of the **[4]ER** in **2.49** results in the most dramatic spectral changes; two new absorptions appear in the lower energy region of **2.49** at ca. $\lambda_{\text{max}} = 495$ and $\lambda_{\text{max}} = 542$ nm, the origin of which has not yet been determined.

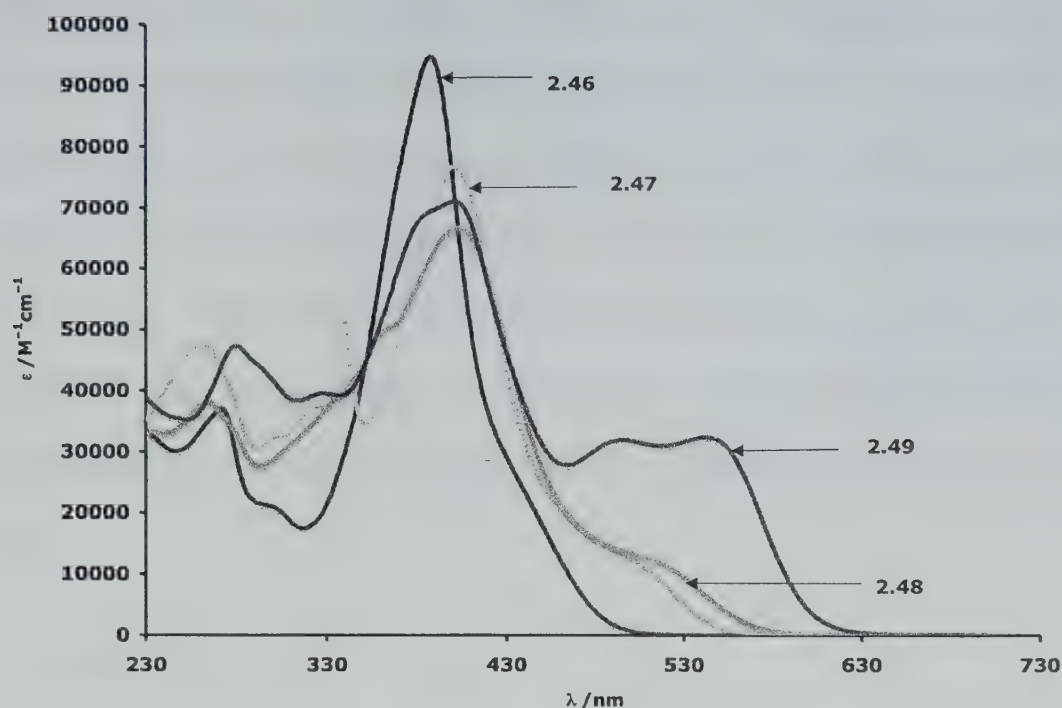


Figure 3-11 UV-vis spectra of **2.46-2.49** in CH₂Cl₂

Table 3-6 UV-Vis spectral data of **2.46-2.49** in CH₂Cl₂

Compound	$\lambda_{\text{max}} / \text{nm}$ ($\epsilon = [\text{M}^{-1} \text{cm}^{-1}]$)			
2.46	430 (sh, 29 100)	393 (94 900)	272 (37 000)	—
2.47	498 (sh, 13 200)	401 (76 800)	339 (52 300)	261 (48 000)
2.48	497 (sh, 13 700)	402 (66 800)	264 (38 300)	—
2.49	542 (32 400)	495 (31 700)	401 (71 100)	280 (47 400)

A comparison of the lowest energy λ_{max} [**4**]ERs **2.47-2.49** (Figure 3-12) with the corresponding acyclic oligomers **2.55**, **2.54**, and **2.59**, featuring the same longest linearly conjugated segments, shows bathochromic shifts of 50, 37 and 67 nm, respectively. The bathochromic shift observed upon cyclization may be attributed to macrocyclic cross-

conjugation, which is consistent with the work of Diederich on similar systems.^{4c} The increase in bathochromic shifts upon going from TIPS substituents to diisopropylanilino substituents on the periphery or the [4]ERs is also in agreement with the findings of Diederich and coworkers.^{4c} The authors also state that macrocyclic cross-conjugation becomes increasingly efficient on going from trialkylsilyl substituents to strongly electron-donating substituents on the periphery of perethynylated ERs.^{4c}

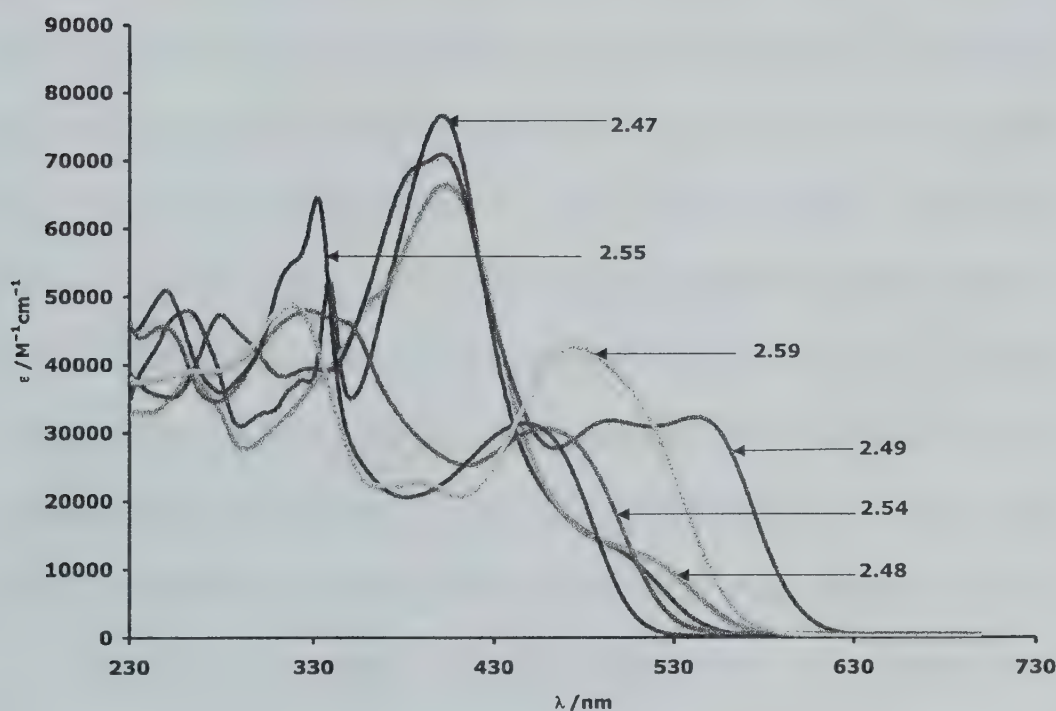


Figure 3-12 UV-vis spectra of 2.47-2.49, 2.54, 2.55 and 2.59 in CH_2Cl_2

3.3.2.3 Electrochemical properties

The electrochemical studies were conducted in collaboration with fellow group member Mr. Adrian Murray and the results are summarized in Table 3-7. Compounds **2.46**, **2.48**, and **2.49** each show two one-electron reduction steps, where the first is reversible and the second is not as well defined. For compound **2.47**, two reversible one-electron reduction steps are observed. Decoration with nitrophenyl or benzonitrile groups results in an anodic shift of the first reduction potential relative to that of **2.46**. As expected, the introduction of diisopropylaniline groups as in **2.49** results in no significant change of the first reduction potential but a substantial decrease in the first oxidation potential in comparison to unsubstituted **2.46**. Compounds **2.46-2.48** show a single, quasi-reversible, one-electron oxidation step at nearly identical potentials. It is worthy to note that the first oxidation potential of **2.49** (0.32 V) and **2.59** (0.33 V) are nearly identical, indicating that it is likely that the anilino group is being oxidized. The first reduction potential of **2.48** (−1.56 V) is similar to that of nitrobenzene (1.61 V)^{7a} indicating it is likely that the nitrophenyl group is being reduced.

The electrochemical HOMO-LUMO gaps of **2.46-2.48** are calculated as the difference of the first oxidation and reduction potentials and are listed in Table 3-7. The electrochemical HOMO-LUMO gap of **2.46** ($E_g^{\text{electro}} = 2.57$ eV) and **2.47** ($E_g^{\text{electro}} = 2.31$ eV) are lower than that of the corresponding acyclic precursors **2.53** ($E_g^{\text{electro}} = 2.87$ eV) and **2.55** ($E_g^{\text{electro}} = 2.31$ eV, see Table 3-4), respectively. Conversely, **2.48** (E_g^{electro}

= 2.52 eV) has a higher electrochemical HOMO-LUMO gap than that of its corresponding acyclic precursor **2.54** ($E_g^{\text{electro}} = 2.10$ eV). Interestingly, no significant lowering of the electrochemical HOMO-LUMO is observed for **2.49** ($E_g^{\text{electro}} = 2.08$ eV), despite its lower energy absorption in the UV-Vis region, as compared to its acyclic precursor **2.59** (2.13 eV). Overall, the redox behavior of **2.47-2.49** resembles that of the corresponding *iso*-PDAs and this leads to the conclusion that the donor and acceptor groups behave as independent redox centers.^{4b,f} In other words, after the first electron-transfer has occurred, additional redox centers are not affected and therefore, subsequent electron transfers give rise to potentials characteristic of the unsubstituted analog (i.e. **2.46**).

Table 3-7 Summary of redox data for **2.46-2.49**^a

Compound	E_{red1}	E_{red2}	E_{red3}	E_{ox1}	E_{ox2}	E_{ox3}	E_g^{electro}
	<i>V</i>	<i>V</i>	<i>V</i>	<i>V</i>	<i>V</i>	<i>V</i>	<i>eV</i> ^c
2.46	-1.75	-2.04	—	0.83	—	—	2.57
2.47	-1.46	-1.77	—	0.85	1.06	—	2.31
2.48	-1.56	—	—	0.80	—	—	2.52
2.49	-1.75	-2.15	—	0.32 ^b	0.77 ^b	—	2.08

^a In deoxygenated CH_2Cl_2 on a Pt working electrode with a Ag/Ag^+ pseudoreference (0.01 M AgNO_3 , 0.1 M Bu_4NPF_6 in CH_3CN), and a Pt coil as counter electrode; Fc^+/Fc reference. ^b Peak potential, E° , for irreversible waves are estimated as $E^\circ = (E_{\text{peak}} + E_{\text{onset}})/2$. ^c Electrochemical HOMO-LUMO gap, $(E_{\text{ox1}} - E_{\text{red1}})$.

3.3.2.4 Emission properties

Emission spectra have been measured in deoxygenated CH_2Cl_2 with an excitation wavelength of 425 nm (Figure 3-13) and the results are summarized in Table 3-8. All **[4]ERs** show a single broad emission peak, and the relative intensity shows marked dependence on the nature of the appended groups. The introduction of electron-donating and electron-withdrawing substituents into the periphery of the radialene leads to an increase in relative intensities, in comparison to, for example, **2.46**. Furthermore, strongly electron-donating substituents enhance emission more than strongly electron-withdrawing substituents. This observation is consistent with that reported by Haley for TPEBs¹⁰ and Diederich for TEEs.⁴ The maximum emission wavelength (λ_{em}) shifts toward lower-energy on going from **2.46** (λ_{em} = 565 nm) to **2.49** (λ_{em} = 628 nm). The maximum emission wavelength of compounds **2.46-2.47** are all red-shifted in comparison to the corresponding *iso*-PDAs **2.53** (λ_{em} = 487 nm), **2.55** (λ_{em} = 538 nm), **2.54** (λ_{em} = 566 nm), and **2.59** (λ_{em} = 609 nm), respectively. The degree of red-shift of λ_{em} for the **[4]ERs** as compared to that of the corresponding *iso*-PDAs match closely with the bathochromic shifts of the lowest energy λ_{max} observed upon going from the acyclic to cyclic systems. The observed Stokes shift also shows a strong dependence on the nature of the substituents in the periphery of the **[4]ER**, being highest for **2.46** (135 nm) and lowest for **2.49** (86 nm). In the case of **2.49**, the aniline residues may serve to rigidify the framework of

the [4]ER via electron donation to the radialene core and, thus, a smaller Stokes shift is observed. This is in agreement with the results obtained from UV-Vis where the most red-shifted λ_{max} is observed for **2.49** and while the most blue-shifted λ_{max} is observed for **2.46**. The emission wavelength does not vary as function of excitation wavelength (λ_{exc} = 364, 385, or 400 nm) suggesting that emission occurs from similar excited states for **2.46**. This statement is also true for **2.47-2.49**.

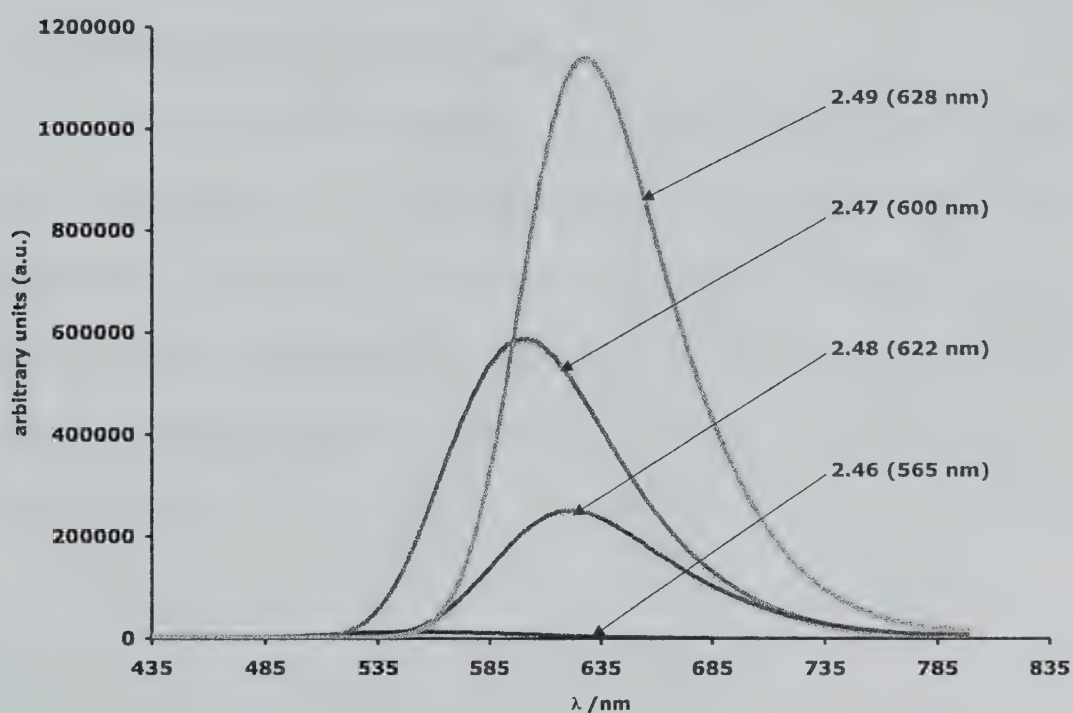


Figure 3-13 Emission spectra of **2.46-2.49** in CH_2Cl_2 ; λ_{em} [nm] for each [4]ER is shown in parentheses

Table 3-8 Qualitative fluorescence data of **2.46-2.49** in CH₂Cl₂^a

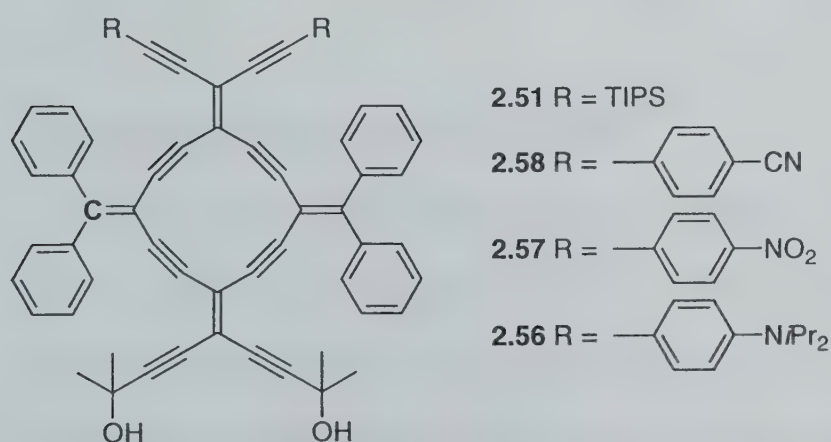
Compound	λ_{in} /nm ^b	λ_{max} /nm ^c	λ_{em} /nm	Stokes Shift /nm
2.46	393	430	565	135
2.47	401	498	600	102
2.48	402	497	622	125
2.49	495	542	628	86

^a λ_{exc} = 425 nm. ^b Wavelength of most intense absorption beyond 400 nm. ^c

Lowest-energy absorption maxima.

3.3.3 [4]ERs based on *iso*-PDA 2.53

A second series of [4]ERs **2.51** and **2.56-2.58** (Figure 3-14) have been investigated for structure-property relationships using cyclic voltammetry, ¹³C NMR, UV-Vis and fluorescence spectroscopies. It was envisioned that **2.56-2.58** would allow for direct comparisons to be made with the corresponding D-A systems and therefore, give insight into the electronic communication between donor and acceptor.

**Figure 3-14** [4]ERs based on **2.51**

3.3.3.1 Physical properties

[4]ERs **2.51** and **2.56-2.58** (Figure 3-14) are solids that exhibit thermal stability up to and beyond 200 °C based on melting point determination and DSC analysis. In particular, **2.56** and **2.57** show decomposition points of ca. 234 and 190 °C, respectively. HR mass spectrometric and ¹H- and ¹³C NMR spectroscopic data for **2.51** and **2.56-2.58** are consistent with the structures proposed. A consistent shift of particular resonances is observed upon cyclization. For example, the vinylidene carbon (Ph₂C=C) shifts upfield from 158.6 ppm (**2.53**) to 153.4 ppm (**2.51**), from 158.0 ppm (**2.59**) to 153.2 ppm (**2.56**), from 160 ppm (**2.54**) to 155.8 ppm (**2.58**), and from 160.0 ppm (**2.55**) to 155.6 ppm (**2.58**). As seen for the model series of [4]ERs, the ¹³C NMR spectra of **2.51** and **2.5-2.58** do not show chemical shift degeneracy. ¹³C spectroscopic analysis shows 26, 30, 28, and 29 resonances for **2.51** and **2.56-2.58**, respectively.

3.3.3.2 Electronic absorption properties

The electronic absorption behavior of [4]ERs **2.51** and **2.56-2.58** has been explored in CH₂Cl₂ solutions at room temperature and the results are summarized in Figure 3-15 and Table 3-9. Compounds **2.51** and **2.56-2.58** share the common feature of having a major absorption at ca. 400 nm. The spectra of compounds **2.51** and **2.57**, and **2.58** have shoulder absorptions visible at ca. 436, 499 and 494 nm, respectively. As

seen for radialene **2.49**, the introduction of diisopropylaniline groups leads to significant changes in the electronic absorption behavior. Thus, two additional absorptions appear at ca. 488 and 544 nm in the spectrum of **[4]ER 2.56**.

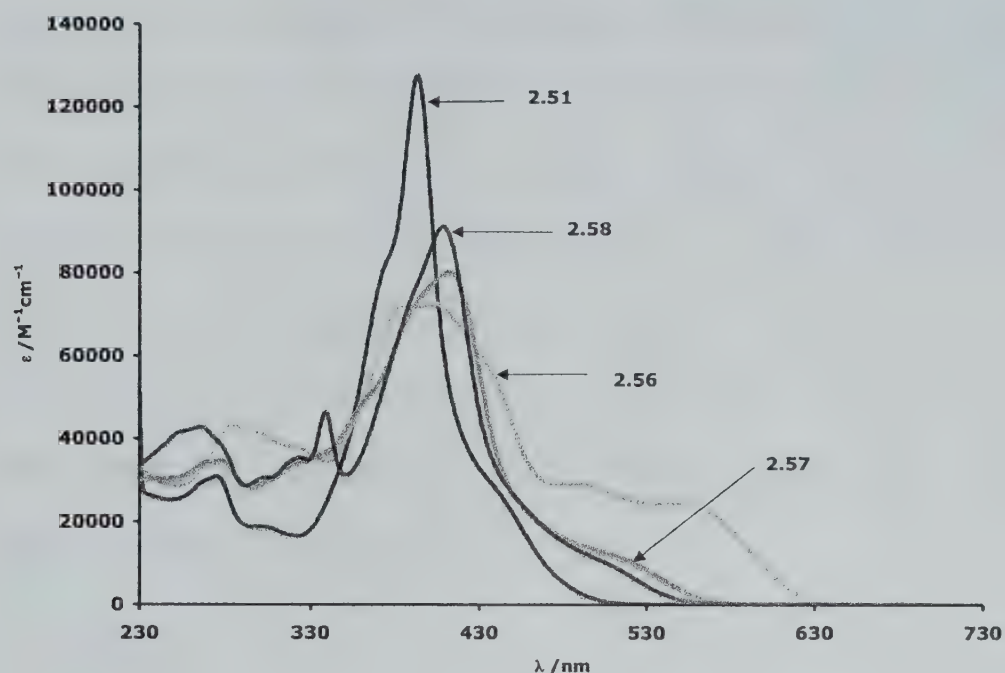


Figure 3-15 UV-Vis spectra of **2.51**, and **2.56-2.58** in CH₂Cl₂

Table 3-9 Summary of UV-Vis spectral data of **2.51**, and **2.56-2.58**

[4]ER	$\lambda_{\text{max}} / \text{nm}$ ($\epsilon = [\text{M}^{-1} \text{cm}^{-1}]$)					
2.51	436	393	275	—	—	—
	(sh, 29 900)	(128 000)	(31 000)			
2.56	544	488	397	387	312	283
	(25 100)	(29 900)	(72 600)	(73 000)	(39 500)	(44 100)
2.57	499	412	277	—	—	—
	(sh, 13 400)	(80 300)	(34 800)			
2.58	494	408	339	—	—	—
	(sh, 12 200)	(91 300)	(46 400)			

A comparison of the lowest energy λ_{max} of **2.51**, and **2.56-2.58** (Table 3-9) to **2.53**, **2.59**, **2.54**, and **2.55** (see Table 3-3, Figure 3-16), respectively, reveals bathochromic shifts of 41, 69, 39, and 46 nm, respectively. Conversely, a comparison of the **[4]ERs** in the model series **2.47-2.49** to their analogs in the series **2.56-2.58** shows that essentially no change is observed in the lowest energy absorption values. This result is expected because the molecules being compared have the identical longest linearly-conjugated segment. As with the model series **2.47-2.49**, the bathochromic shift observed upon cyclization may be attributed to macrocyclic cross-conjugation effects that increase on going from the TIPS-acetonide substituents in **2.51** to the strongly electron-donating diisopropylaniline groups in **2.56**.^{4c}

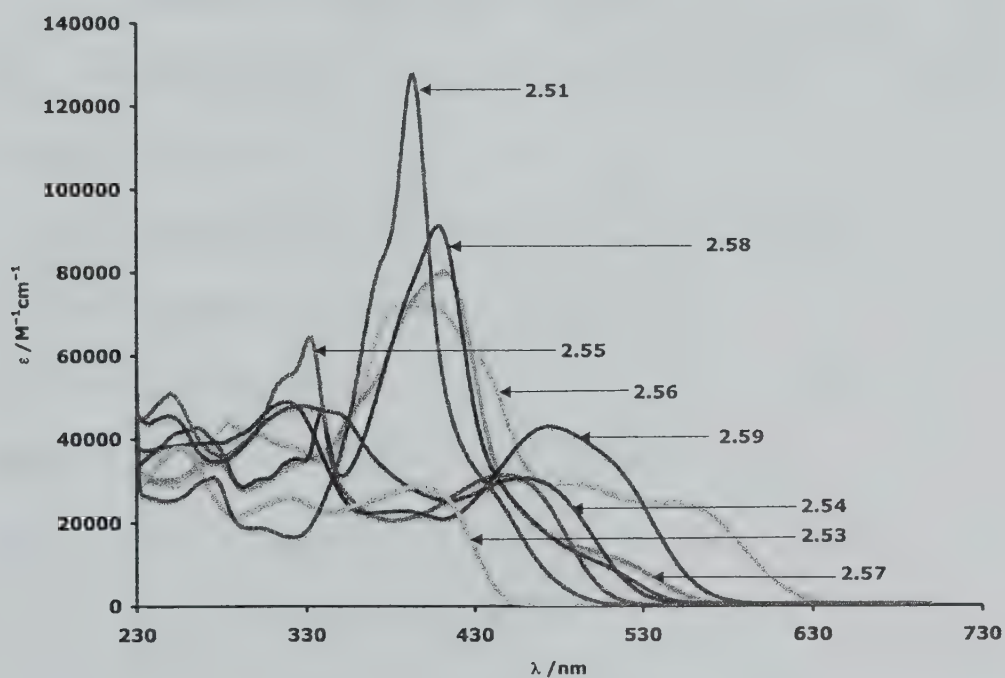


Figure 3-16 UV-Vis spectra of *iso*-PDAs **2.53-2.55**, **2.59** and **[4]ERs 2.51** and **2.56-2.58** in CH₂Cl₂

3.3.3.3 Electrochemical properties

The electrochemical properties of **2.51** and **2.56-2.58** have been investigated by cyclic voltammetry in collaboration with Mr. Adrian Murray and the results are summarized in Table 3-10. For compound **2.51**, three one-electron, reduction steps are observed, the first reversible event is at -1.41 V and the other two reductions are less well-defined at -1.76 and -2.02 V. Decoration of the radialene skeleton with diisopropylaniline groups causes a dramatic decrease of the first oxidation potential from 0.89 V for **2.51** to 0.33 for **2.56**. The introduction of nitrophenyl and benzonitrile groups, as in **2.57** and **2.58**, has no significant effect on the first reduction potential in comparison to **2.51**. The reduction waves for **2.58** are fully reversible while that of **2.56** and **2.57** are quasi-reversible.

It is noteworthy that the first oxidation potential of **2.56** is similar to that of **[4]ER 2.49** (0.32 V) and *iso*-PDA **2.59** (0.33 V) while the first reduction potential of **2.57** (1.36 V) is similar to that of **2.48** (-1.39 V) as well as the nitrophenyl *gem*-substituted TEE **A** (-1.38 V). With the exception of **2.58**, the oxidation waves observed for **2.51**, **2.56**, and **2.57** are irreversible. A comparison of the first reduction potentials of **[4]ERs 2.51** and **2.57-2.58** to model **[4]ERs 2.46-2.48** deserves some attention. The first reduction potential of **2.46** (-1.75 V) is lower than that of **2.51** (-1.41 V). While there is little to no difference observed for **2.47** (-1.46 V) and **2.58** (-1.41), a significant decrease in first reduction potential is observed for **2.48** (-1.56 V) relative to that of **2.57** (-1.36 V).

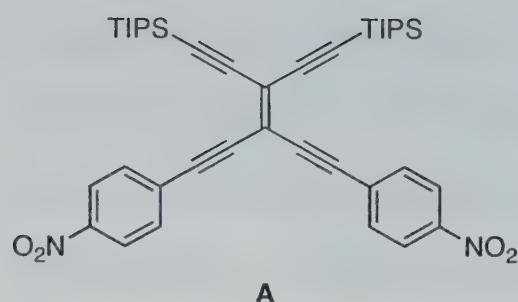


Table 3-10 Summary of redox data for **2.51** and **2.56-2.58**^a

Compound	E_{red1}	E_{red2}	E_{red3}	E_{ox1}	E_{ox2}	E_{ox3}	$E_{\text{g}}^{\text{electro}}$
	<i>N</i>	<i>N</i>	<i>N</i>	<i>N</i>	<i>N</i>	<i>N</i>	/eV ^c
2.51	-1.41	-1.76	-2.02	0.89 ^b	—	—	2.30
2.56	-1.68	-2.09	—	0.33 ^b	0.49 ^b	—	2.01
2.57	-1.36	-1.50	—	1.23 ^b	—	—	2.59
2.58	-1.41	-1.69	—	1.40	—	—	2.82

^a In deoxygenated CH_2Cl_2 on a Pt working electrode with a Ag/Ag^+ pseudoreference (0.01 M AgNO_3 , 0.1 M Bu_4NPF_6 in CH_3CN), and a Pt coil as counter electrode; Fc^+/Fc reference. ^b Peak potential, E° , for irreversible waves are estimated as $E^\circ = (E_{\text{peak}} + E_{\text{onset}})/2$. ^c Electrochemical HOMO-LUMO gap, $(E_{\text{ox1}} - E_{\text{red1}})$.

3.3.3.4 Emission properties

Emission spectra have been measured in deoxygenated CH_2Cl_2 with an excitation wavelength of 425 nm and the results are summarized in Figure 3-17 and Table 3-11. In comparison to **2.56-2.58**, **2.51** shows a vanishingly small emission centered at 519 nm. Compounds **2.56-2.58** show a single broad emission peak whose relative intensity depends on the nature of the substituents on the periphery. Donor-substitution increases the relative-intensity more than does acceptor-substitution (**2.57**

or **2.58**). A similar observation has been made for the model series of **[4]ERs** (Figure 3-13). The maximum emission wavelength (λ_{em}) shifts toward lower-energy upon donor- and acceptor substitution reaching a maximum of $\lambda_{em} = 659$ nm for donor-substituted **2.56**. A bathochromic shift of the maximum emission wavelength is observed when comparing **2.51** and **2.56-2.58** to the corresponding *iso*-PDAs **2.53** (487 nm), **2.59** (609 nm), **2.54** (566 nm) and **2.55** (538 nm). Interestingly, λ_{em} of **2.51** (519 nm), **2.58** (577 nm), and **2.57** (595 nm) are all blue-shifted as compared to that of **2.46** (565 nm), **2.47** (600 nm) and **2.48** (622 nm).

The observed Stokes shift for **[ERs] 2.51** and **2.56-2.58** (Table 3-11) also shows a strong dependence on the nature of the appended group. It is noteworthy that the largest Stokes shift is seen for **2.56**, which also has the highest λ_{em} and λ_{max} for this series of molecules. The emission wavelength does not vary as function of excitation wavelength ($\lambda_{exc} = 364, 385, \text{ or } 400$ nm), suggesting that emission occurs from similar excited state for **2.51**. A similar conclusion can be drawn for **[4]ERs 2.56-2.58**.

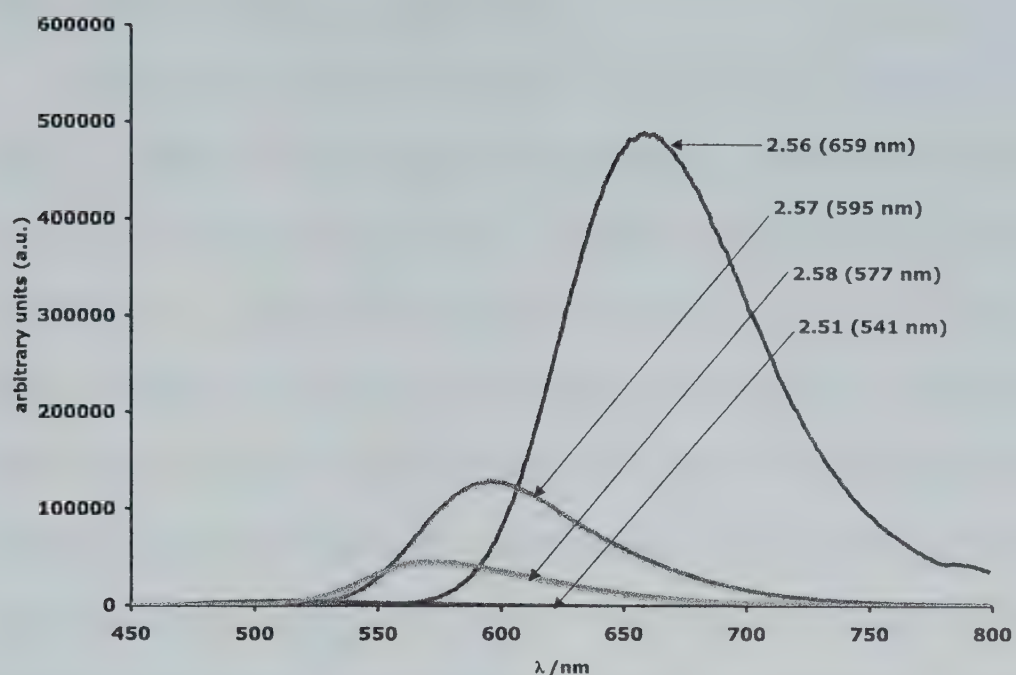


Figure 3-17 Emission spectra of **2.51** and **2.56-2.58** in CH_2Cl_2 (excitation at 425 nm); λ_{em} [nm] for each **[4]ER** is shown in parentheses

Table 3-11 Summary of qualitative fluorescence data of **2.51** and **2.56-2.58** in CH_2Cl_2 ^a

Compound	λ_{in} /nm ^b	λ_{max} /nm ^c	λ_{em} /nm	Stokes Shift /nm
2.51	393	436	519	83
2.56	488	544	659	115
2.57	412	499	595	96
2.58	408	494	577	83

^a $\lambda_{\text{exc}} = 425 \text{ nm}$ ^b Wavelength of most intense absorption. ^c Lowest-energy absorption maxima.

3.3.4 [4]ERs based on *iso*-PDA 2.59

Compounds **2.52** and **2.60-2.62** (Figure 3-18) comprise the last series of [4]ERs to be investigated for structure-property relationships with the aid of DSC, cyclic voltammetry, ^{13}C NMR, UV-Vis, and fluorescence spectroscopies. Comparison of the D-A [4]ERs to the corresponding *iso*-PDAs or to the D- or A-substituted [4]ERs will shed light on whether, the electronic properties of D-A systems are a sum of the constituent parts or whether they are influenced by each other and give rise to new and interesting features. Previous work in the Tykwinski group on donor-acceptor end-capped *iso*-PDAs^{8a} and *gem*-DEEs^{8b} has already shown that their properties are different from the corresponding donor- or acceptor-substituted systems alone.

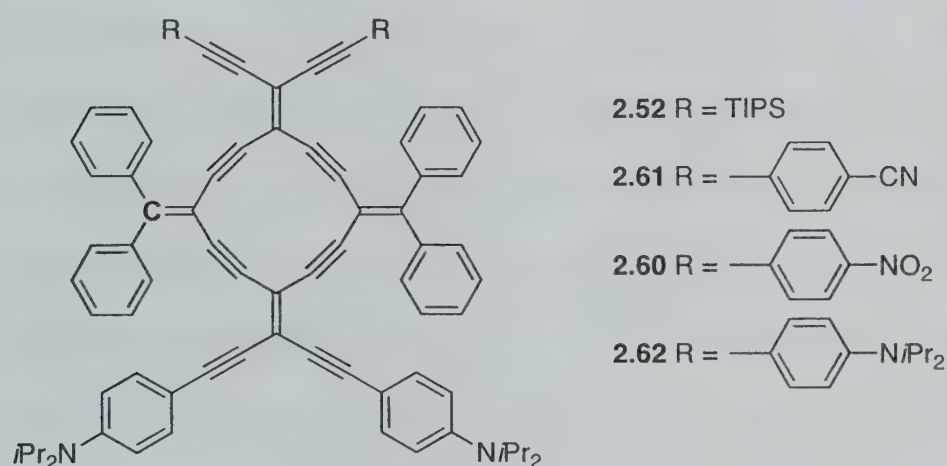


Figure 3-18 Donor, donor-acceptor, and donor-donor [4]ERs

3.3.4.1 Physical properties

[4]ERs **2.52** and **2.60-2.62** demonstrate perhaps surprising thermal stability with decomposition points ranging from 247 °C for **2.52** up to 287 °C for **2.62** that have been confirmed using DSC. The ^1H - and ^{13}C NMR spectroscopic data of **2.52** and **2.60-2.62** are consistent with the proposed structures. For example, analysis of the ^{13}C NMR spectrum of **2.52** shows 30 signals corresponding to 30 unique carbons while that of **2.62** has 18 resonances corresponding to the 18 unique carbons in their structures. HR mass spectrometry ultimately provided confirmation of the molecular formulae expected for **2.52** and **2.60-2.62**.

There is no significant change in the chemical shift of the diagnostic exocyclic vinylidene carbon atom ($\text{Ph}_2\text{C}=\text{C}$) upon donor/acceptor substitution. For example, this carbon appears at 153, 154, 154 and 152 ppm in the ^{13}C NMR spectra of **2.52**, **2.60-2.62**, respectively. It is worthy to note that these chemical shifts agree closely with the chemical shift 152 ppm that was observed for the exocyclic vinylidene carbon atom of the perphenylated [4]ER **2.63** (Figure 3-19).^{2b} The chemical shift this carbon atom in **2.52** ($\text{Ph}_2\text{C}=\text{C}$) shifts upfield by ca. 5 ppm relative to that of the vinylidene carbon atom outside the main chain of *iso*-PDA **2.59** (Figure 3-19) found at 158.0 ppm. Similarly, for D-A **2.60** this carbon atom ($\text{Ph}_2\text{C}=\text{C}$) shifts upfield by ca. 6 and 4 ppm as compared to **2.54** (160.0 ppm) and **2.59**, respectively. A similar observation has been made for this carbon

atom found in **2.61** (154.0 ppm) when compared to that of *iso*-PDAs **2.55** (160.0 ppm) and **2.59**.

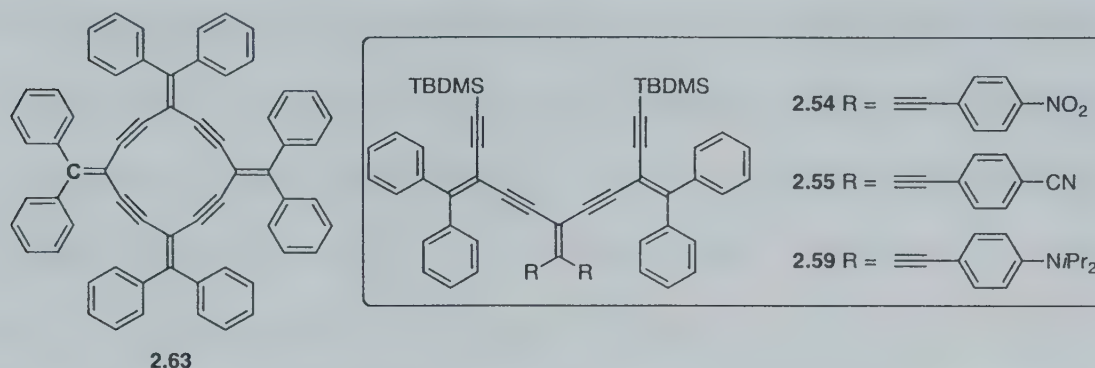


Figure 3-19 Perphenylated [4]ER **2.63** and *iso*-PDAs **2.54**, **2.55**, and **2.59**

3.3.4.2 Electronic absorption properties

The electronic absorption behavior of *iso*-PDAs **2.52** and **2.60-2.62** have been investigated by UV-Vis spectroscopy in CH_2Cl_2 at room temperature, and the results are summarized in Figure 3-20 and Table 3-12. The spectrum of **2.52** has two major maxima centered at 388 nm ($\epsilon = 76\,400\text{ M}^{-1}\text{cm}^{-1}$) and 292 nm ($\epsilon = 48\,200\text{ M}^{-1}\text{cm}^{-1}$) in the UV region. At least three shoulder absorptions can be identified in the lower energy region of the spectrum of **2.52** at 541 nm ($\epsilon = 24\,500\text{ M}^{-1}\text{cm}^{-1}$), 485 nm ($\epsilon = 32\,200\text{ M}^{-1}\text{cm}^{-1}$), and 438 nm ($\epsilon = 61\,900\text{ M}^{-1}\text{cm}^{-1}$).

[4]ERs **2.60-2.62** share the common feature of three major absorptions and a lower energy shoulder absorption at similar energies. The absorptions in the spectra of D-A substituted **2.60** and **2.61** are all at similar energies including the shoulder absorption at 582 and 573 nm, respectively. Interestingly, the introduction of two additional

diisopropylaniline groups (**2.62**) onto the radialene leads to a change in molar absorptivities but not energies of the two low energy absorptions at ca. 542 and 485 nm in comparison to **2.52**. Thus, it seems clear that these absorptions are related to the presence of the anilino group in combination with the electron-deficient **[4]ER** core. This trend can also be extended to **[4]ERs 2.49** ($\lambda_{\text{max}} = 542 \text{ nm}$, $\epsilon = 32\,400 \text{ M}^{-1}\text{cm}^{-1}$) and **2.56** ($\lambda_{\text{max}} = 544 \text{ nm}$, $\epsilon = 25\,100 \text{ M}^{-1}\text{cm}^{-1}$), in comparison to **2.52** ($\lambda_{\text{max}} = 542 \text{ nm}$, $\epsilon = 24\,500 \text{ M}^{-1}\text{cm}^{-1}$) and **2.62** ($\lambda_{\text{max}} = 545 \text{ nm}$, $\epsilon = 59\,400 \text{ M}^{-1}\text{cm}^{-1}$). Clearly, however, cyclization to the **[4]ER** skeleton plays a major role, as λ_{max} for **2.59** is observed at 475 nm, with evidence of a shoulder at ca. 500 nm. Consequently, the origin of the lowest energy absorption is most likely due to macrocyclic cross-conjugation.^{4c} However, further theoretical investigations are needed to confirm this and to provide more insight into the electronic communication in these novel *2D*-conjugated systems.

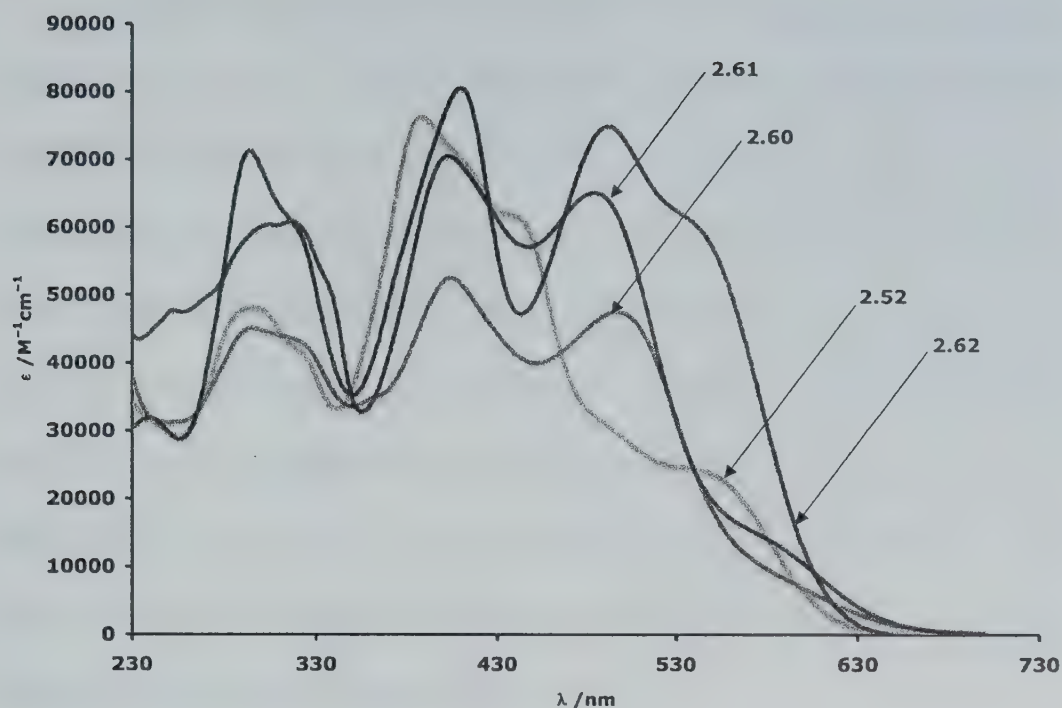
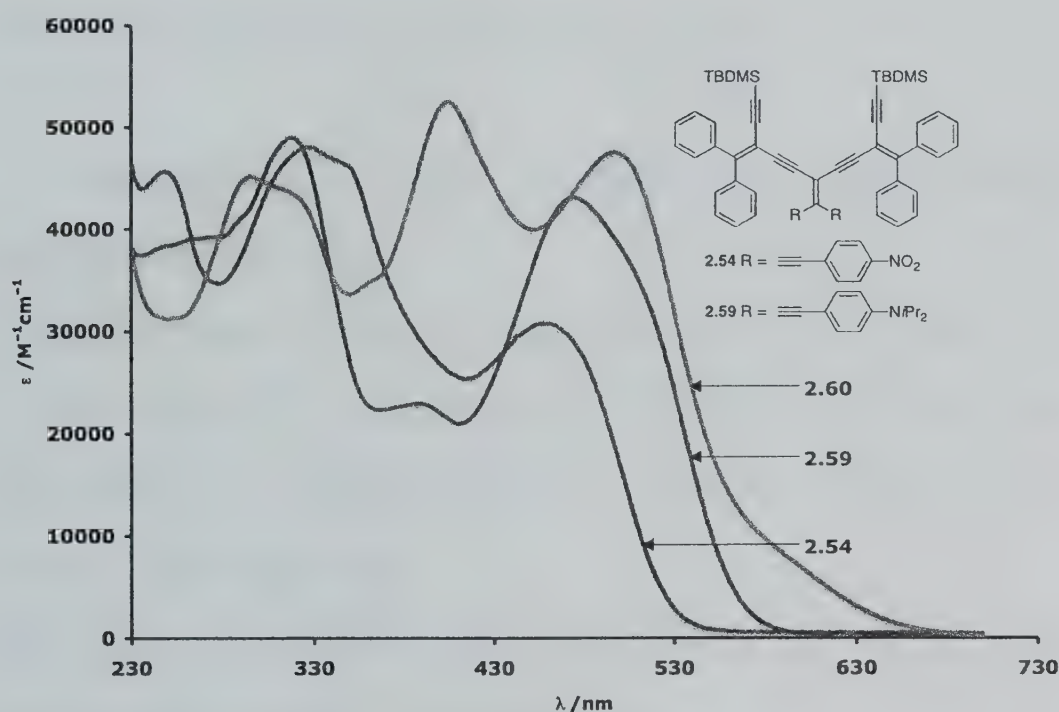


Figure 3-20 UV-vis spectra of 2.52 and 2.60-2.62 in CH₂Cl₂

Table 3-12 UV-Vis spectral data of 2.52 and 2.60-2.62 in CH₂Cl₂

[4]ER		$\lambda_{\text{max}} / \text{nm} (\epsilon = [\text{M}^{-1} \text{cm}^{-1}])$			
2.52	542	485	438	388	292
	(sh, 24 500)	(32 200)	(61 900)	(76 400)	(48 200)
2.60	582	497	404	295	—
	(sh, 9 470)	(47 600)	(52 600)	(45 300)	
2.61	573	485	403	317	—
	(sh, 15 200)	(65 200)	(70 300)	(61 100)	
2.62	545	492	408	293	—
	(sh, (59 400)	(75 000)	(80 500)	(72 000)	

A comparison of the UV-Vis spectrum of D-A substituted **2.60** to its constituent parts, i.e., donor-substituted *iso*-PDA **2.59** and acceptor-substituted *iso*-PDA **2.54** (Figure 3-21), reveals that **2.60** is clearly different than the sum of its parts, with a low energy tail/shoulder that is not present in either *iso*-PDA. A similar observation has been made before for donor-acceptor substituted *iso*-PDAs.^{8a} Likewise, a comparison of the spectrum for D-A **[4]ER 2.60** to that of donor **[4]ER 2.56** and acceptor **[4]ER 2.57** (Figure 3-22) reveals that the shoulder absorption of **2.60** (582 nm) falls at the lowest energy, although lowest energy absorption for **2.56** (544 nm) is considerably more intense.



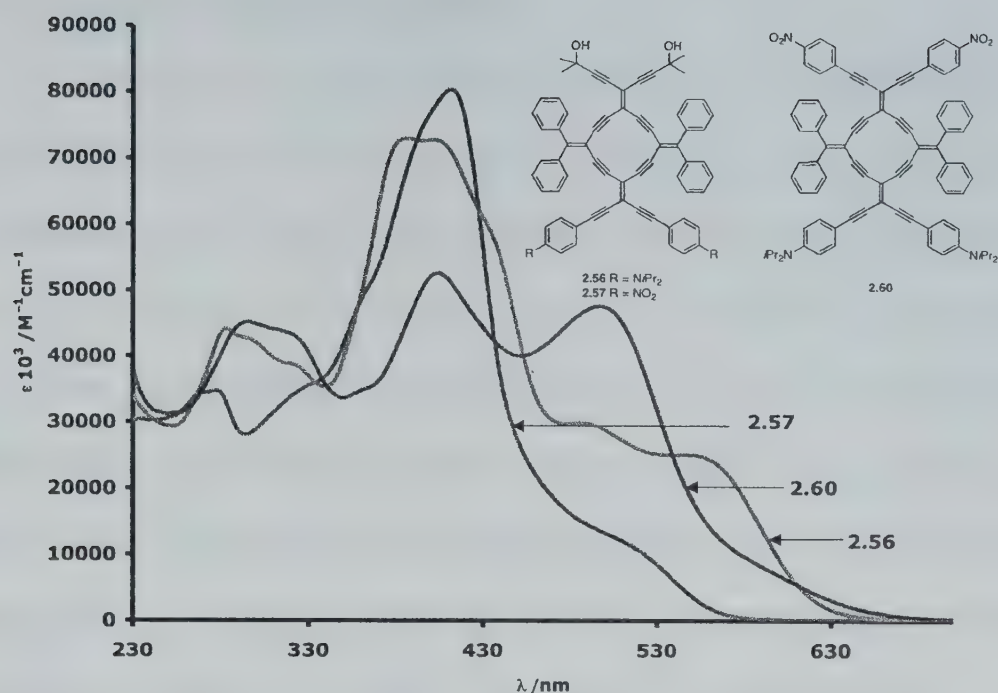


Figure 3-22 UV-vis spectra of **2.56**, **2.57**, and **2.60** in CH₂Cl₂

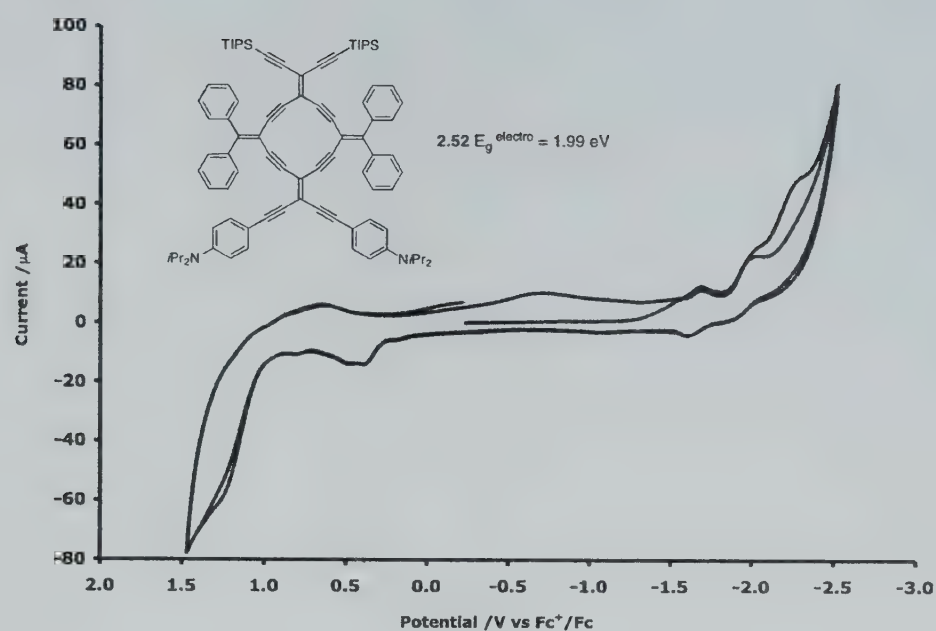
The following general trends emerge from the UV-Vis spectroscopic comparisons made so far:

- (1) Macrocyclization leads to a bathochromic shift of the lowest energy λ_{max} in comparison to the corresponding *iso*-PDAs. Donor-substituted *iso*-PDAs give rise to a larger bathochromic shift upon cyclization than do acceptor substituted-analogs.
- (2) Donor-substituted **[4]ERs** show red-shifted lowest energy λ_{max} values in comparison to acceptor-substituted **[4]ERs**
- (3) Donor-acceptor substitution leads to a further bathochromic shift of the lowest energy λ_{max} than does either donor- or acceptor-substitution alone.

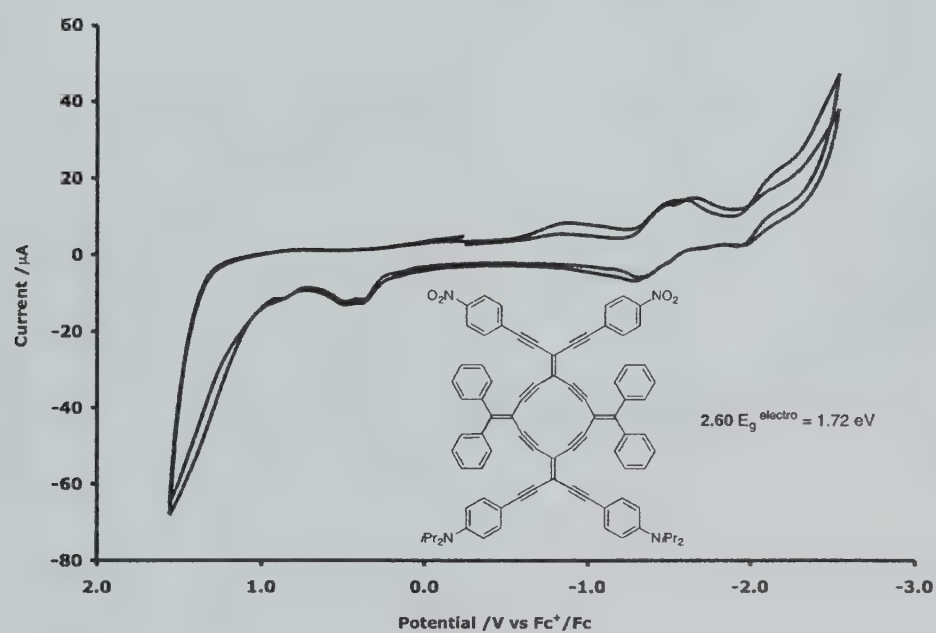
3.3.4.3 Electrochemical properties

The electrochemical redox properties of **2.52** and **2.60-2.62** have been measured in CH₂Cl₂ by cyclic voltammetry (Figure 3-23 a-d) in collaboration with fellow group member, Mr. Adrian Murray and the results are summarized in Table 3-13. Compound **2.52** has two quasi-reversible, one-electron reduction steps at -1.65 V and -1.95 V, and two irreversible, one-electron oxidation steps at 0.34 V and 0.72 V. The introduction of nitrophenyl or benzonitrile groups, as in **2.60** and **2.61**, respectively, significantly shifts the first and second reduction potentials anodically relative to those of **2.52**. The introduction of two diisopropylaniline groups leads to a significant decrease in first reduction potential as compared to **2.52**. It is interesting to note that the introduction of nitrophenyl (**2.60**, 0.32 V), benzonitrile (**2.61**, 0.36 V) or additional diisopropylaniline (**2.62**, 0.32 V) groups does not affect the first oxidation potential throughout the series in comparison to **2.52** (0.34 V).

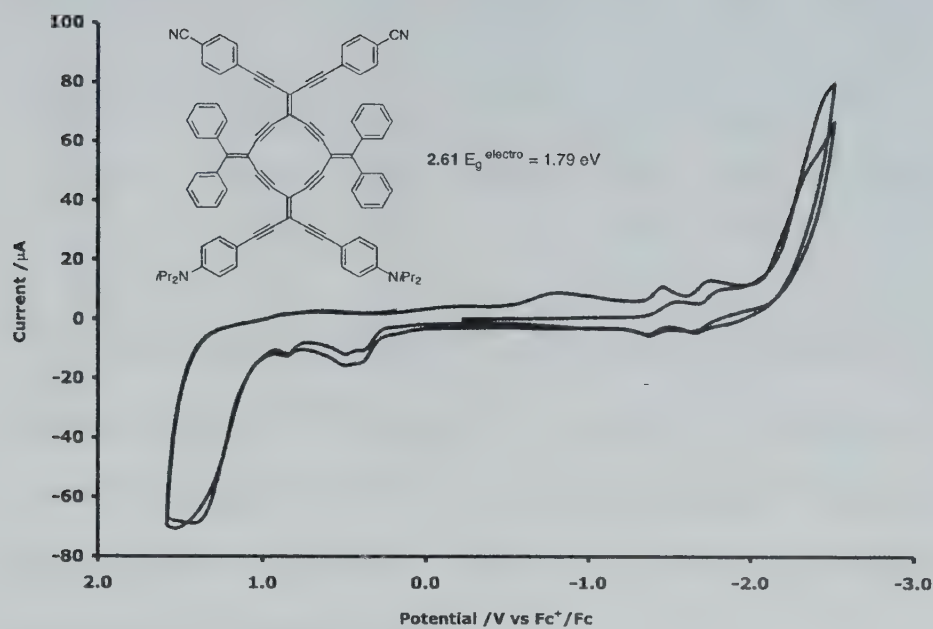
(a)



(b)



(c)



(d)

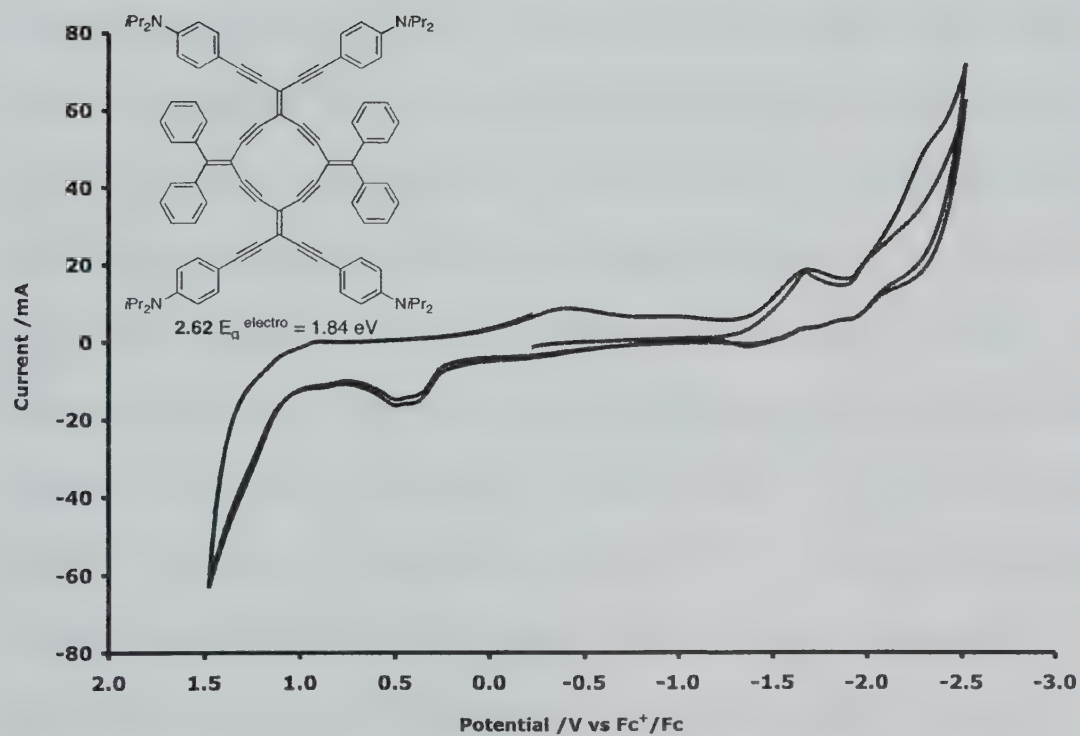


Figure 3-23 Cyclic voltammograms of [4]ERs 2.52 and 2.60-2.62 in CH_2Cl_2

Table 3-13 Electrochemical data of **2.52** and **2.60-2.62** in CH₂Cl₂^a

Compound	E _{red1}	E _{red2}	E _{red3}	E _{ox1}	E _{ox2}	E _{ox3}	E _g ^{electro} /eV ^c
	<i>N</i>	<i>N</i>	<i>N</i>	<i>N</i>	<i>N</i>	<i>N</i>	
2.52	−1.65	−1.95	—	0.34 ^b	0.72 ^b	—	1.99
2.60	−1.40	−1.54	−2.02	0.32 ^b	0.46 ^b	0.82 ^b	1.72
2.61	−1.44	−1.72	—	0.36 ^b	0.76 ^b	—	1.79
2.62	−1.52	−1.98	—	0.32 ^b	0.51 ^d	—	1.84

^a In deoxygenated CH₂Cl₂ on a Pt working electrode with a Ag/Ag⁺ pseudoreference (0.01 M AgNO₃, 0.1 M Bu₄NPF₆ in CH₃CN), and a Pt coil as counter electrode; Fc⁺/Fc reference. ^b Peak potential, E°, for irreversible waves are estimated as E° = (E_{peak} + E_{onset}) / 2. ^c Electrochemical HOMO-LUMO gap, (E_{ox1} − E_{red1}). ^d Oxidation shoulder

Comparing the first and second reduction potentials of acceptor-substituted **[4]ERs 2.57** (−1.36 V and −1.50 V) and **2.58** (−1.40 V and −1.69 V) to those of donor-acceptor substituted **[4]ERs 2.60** (−1.40 V and −1.54 V) and **2.61** (−1.44 V and −1.72 V), respectively, shows that there is little difference brought about by the diisopropylanilino groups. Thus, the reduction processes are dominated by the acceptor groups. The electrochemical data show that there is a lowering of the HOMO-LUMO gap upon introduction of acceptors, as in **2.60** (E_g^{electro} = 1.72 eV) and **2.61** (E_g^{electro} = 1.79 eV), versus that of **2.52** (E_g^{electro} = 1.99 eV). Decoration with two additional diisopropylaniline also leads to a decrease of the electrochemical HOMO-LUMO gap (**2.52**, 1.99 eV vs. **2.62**, 1.84 eV).

A comparison of **[4]ER 2.60** to **[4]ER 2.56** or **2.57** (Figure 3-24) also reveals a lowering of the electrochemical HOMO-LUMO gap. The same can be said for a comparison of **2.61** with **2.58** or **2.57**. These results suggest that the presence of donors and acceptors in a cross-conjugated relationship, as in **2.60** and **2.61** leads to a smaller electrochemical band gap. Furthermore, the strength of the acceptor (**2.60** vs **2.61**) does not seem to have a dramatic effect on the electrochemical band gap. The effect of cyclization on the electrochemical HOMO-LUMO gap shows a marked dependence on the presence of donors or acceptors. For *iso*-PDA **2.59** (2.13 eV), the electrochemical HOMO-LUMO gap essentially remains unchanged as compared to that of **[4]ERs 2.49** (2.08 eV), **2.56** (2.01 eV), or **2.52** (1.99 eV). Conversely, a significant increase of the electrochemical HOMO-LUMO gap is observed on going from **2.54** (2.10 eV) to **2.48** (2.52 eV) and **2.57** (2.59 eV) or **2.55** (2.55 eV) to **2.58** (2.82 eV).

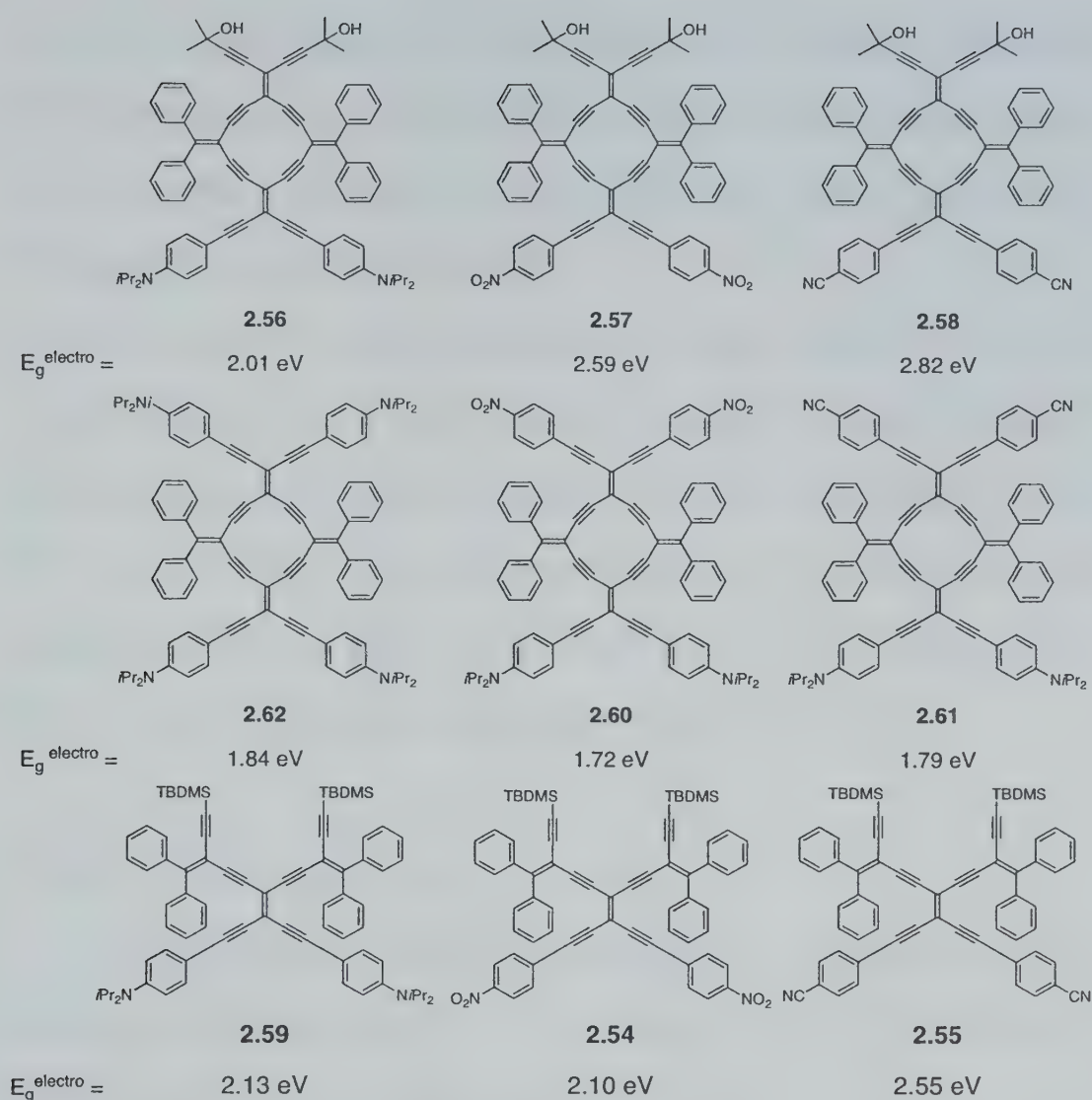


Figure 3-24 Electrochemical band gaps of *iso*-PDAs and [4]ERs

The following general trends emerge from the electrochemical studies:

- (1) Incorporation of donors, as in **2.60** and **2.61**, into the periphery of [4]ERs containing acceptors (**2.57** and **2.58**) leads to a decrease of the first oxidation potential but has little or no effect on the first and second reduction potentials of **2.60** and **2.61**.

(2) Incorporation of acceptors, as in **2.60** and **2.61**, into the periphery of **[4]ERs** bearing donor groups (**2.52** and **2.56**) causes the first and second reduction potential to be shifted anodically while there is essentially no change of the first oxidation potential.

(3) A lowering of the electrochemical band gap is observed for D-A systems relative to that of the corresponding D- or A- substituted **[4]ERs**.

(4) The energy levels of the HOMO and LUMO of D-A **[ERs]** **2.60** and **2.61** resemble those of the individual components. For example, the first reduction potential of **2.60** (−1.40 V) is similar to that of **2.54** (−1.39 V) while its first oxidation potential is similar to that of **2.59** (0.33 V).

3.3.4.4 Emission properties

Emission spectra have been measured in deoxygenated CH₂Cl₂ with an excitation wavelength of 425 nm (Figure 3-25) and the results are summarized in Table 3-14. Much like the other **[4]ERs**, emission varies as a function of the substituents in the periphery. Both **[4]ERs** **2.52** (λ_{em} = 660 nm) and **2.62** (λ_{em} = 650 nm) show a single broad emission peak at similar wavelength, and the Stokes shifts (119 and 105 nm, respectively) are also comparable. The slightly smaller Stokes shift of **2.62** may be attributed to a further rigidification of the **[4]ER** core in the ground state due to the presence of two additional aniline residues and the associated electron donation to the radialene core. The introduction of electron-withdrawing substituents, on the other hand, leads to quenching of the

fluorescence for **2.60** and **2.61**, as has been observed for other acetylenic scaffolds with D-A substituents.^{9,10} The emission wavelength for **2.52** and **2.62** does not vary as a function of excitation wavelength (λ_{exc} = 364, 385, or 400 nm), suggesting that emission occurs from similar excited states for both **[4]ERs**. It is noteworthy that no increase in emission is observed for **2.60** and **2.61** as a function of the excitation wavelength.

When comparing the emission of radialene **2.62** (λ_{em} = 650 nm, Stokes shift = 105 nm) to that of its constituent parts, it can be seen that is similar to **2.56** (λ_{em} = 659 nm, Stokes shift = 115 nm). In comparison to *iso*-PDA **2.59** (λ_{em} = 609 nm, Stokes shift = 134 nm), emission is substantially blue shifted for the acyclic analog. The observation reemphasizes the fact that the photophysical properties of the macrocyclic **[4]ERs** can differ quite substantially from the corresponding acyclic building blocks, even when the longest linearly conjugated segment remains analogous.

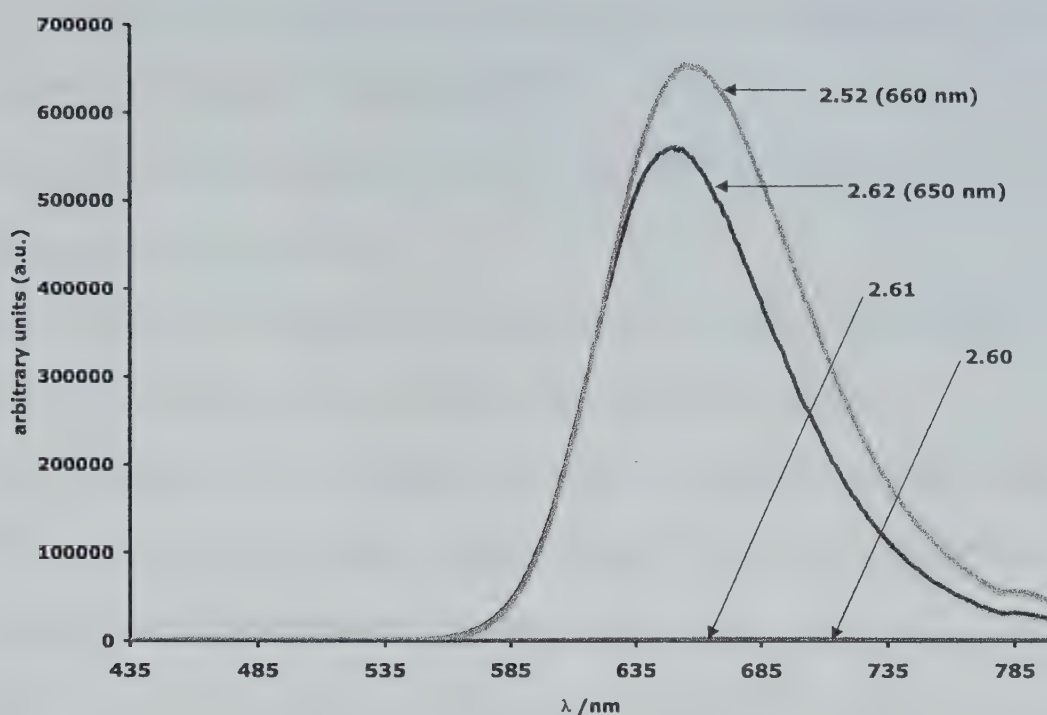


Figure 3-25 Emission spectra of **2.52** and **2.60-2.62** in CH_2Cl_2 (excitation at 425 nm); λ_{em} [nm] for each **[4]ER** is shown in parentheses.

Table 3-14 Summary of qualitative fluorescence data of **2.51** and **2.56-2.62**^a

Compound	λ_{in} /nm ^b	λ_{max} /nm ^c	λ_{em} /nm	Stokes Shift /nm
2.52	388	541	660	119
2.60	404	497	—	—
2.61	403	485	—	—
2.62	408	545	650	105

^a $\lambda_{\text{exc}} = 425 \text{ nm}$ ^b Wavelength of most intense absorption. ^c Lowest-energy absorption maxima.

The following general trends emerge when comparing the emission properties of the *iso*-PDAs and [4]ERs:

- (1) λ_{em} is shifted bathochromically on going from an acyclic *iso*-PDA to the corresponding macrocycle
- (2) The observed Stokes shift decreases upon cyclization, consistent with the more constrained conformation of the radialene framework.
- (3) For both *iso*-PDAs and [4]ERs, the introduction of the strongly-electron donating diisopropylaniline groups causes the relative intensities to increase versus electron-withdrawing groups.
- (4) The presence of donors and acceptors on [4]ER skeleton results in fluorescence quenching.

3.3.4.5 X-Ray crystallography

Crystals of **2.52** suitable for X-ray crystallography have been grown from a CH₂Cl₂ solution of **2.52** which had been layered with hexanes and allowed to slowly evaporate in the refrigerator at 4 °C and an ORTEP drawing is shown in Figure 3-26. Bond lengths for **2.52** are similar to those of other radialenes and are unremarkable.^{2b-c} On the other hand, both the acetylenic and endocyclic alkylidene bond angles are a good measure of the degree of strain in ERs.^{2b} Krebs, in his review on strained cycloalkynes, regarded acetylenic bond angles less than 170° as being strained.^{2d} The crystal structure of **2.52** reveals that the acetylenic bond angles within the macrocyclic core range from 165.5(17)° to 172.5(17)°. In

addition to the acetylene bonds, the endocyclic alkylidene bond angles also give a perspective of strain within the macrocyclic core. The two unique endocyclic alkylidene bond angles based on the TEE fragments are nearly identical at $113.2(14)^\circ$ (C8–C9–C10) to $113.4(14)^\circ$ (C2–C3–C4). Similarly, the two DEE segments (C5–C6–C7 and C11–C12–C1) are also nearly identical at $109.7(14)^\circ$ and $109.5(13)^\circ$. The side view of **2.52** shows evidence of that, while the cyclododeca-1,4,7,10-tetrayne ring is not completely planar, strain resulting from distortion from planarity is not likely to be significant. The torsion angles between the anilino groups (C41–C42–C43–C44–C45–C46 and C53–C54–C55–C56–C57–C58) and the radialene core are ca. 36° and 30° , respectively,¹¹ suggesting that the **[4]ER** core and the appended aniline groups are sufficiently coplanar to allow for electronic communication. This premise is supported the UV-Vis spectra where incorporation of the diisopropylanilino groups leads to a bathochromic shift of the lowest energy λ_{max} . Further justification comes from the smaller Stokes shift observed for the **[4]ER 2.52** as compared to the acyclic precursor **2.59**. The smaller Stokes' shift is characteristic of a more rigid framework, which in turn suggests that electronic communication can be facilitated not only between the appended groups and the cyclic core but also between donors and acceptors.

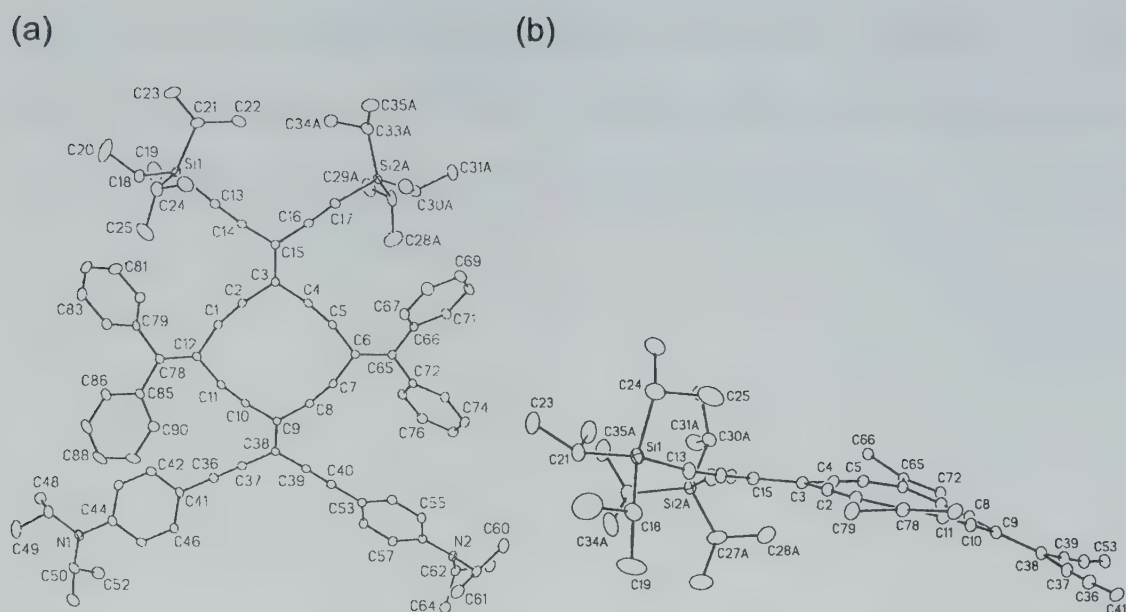


Figure 3-26 ORTEP drawings of **[4]ER 2.52** . (a) Top view and (b) Side view (both at 20% probability level). Selected bond angles (degrees): C1-C2-C3 170.10 (17), C3-C4-C5 171.40 (17), C4-C5-C6 167.38 (17), C6-C7-C8 167.26 (17), C7-C8-C9 168.30 (17), C9-C10-C11 172.50 (17), C10-C11-C12 167.96 (17), C12-C1-C2 165.49 (17), C11-C12-C1 109.49 (13), C2-C3-C4 113.42 (14), C5-C6-C7 109.73 (14), C8-C9-C10 113.15 (14). Hydrogen atoms are not shown and only the ipso carbons of the aromatic groups are shown for b.

A comparison structure of **2.52** to the perphenylated **[4]ER 2.63** (Fig 3-27 a-b) shows that the two structures are comparable^{2b} Acetylenic bond angles within the macrocyclic core of **2.63** range from 166.7(14)° (C1–C2–C3) to 172.2°(15)° (C3–C5–C6) with an average of 169.6°, while both endocyclic alkylidene bond angles are 110.4°. A similar analysis comparing **[4]ER 2.52** to **2.64** (Fig 3-27 c-d)^{2c} shows again that the overall structures are quite comparable. Acetylenic bond angles for **2.64** range from 165.2(3)° (C3–C5–C6) to 170.5(3)° (C1–C2–C3) with an average of

167.7°. The endocyclic alkylidene bond angles that contains a TEE fragment is 112.3(2)° (C2–C3–C5), while that based on the DEE segment (C1'–C7–C6) is slightly smaller at 111.4(3)°.

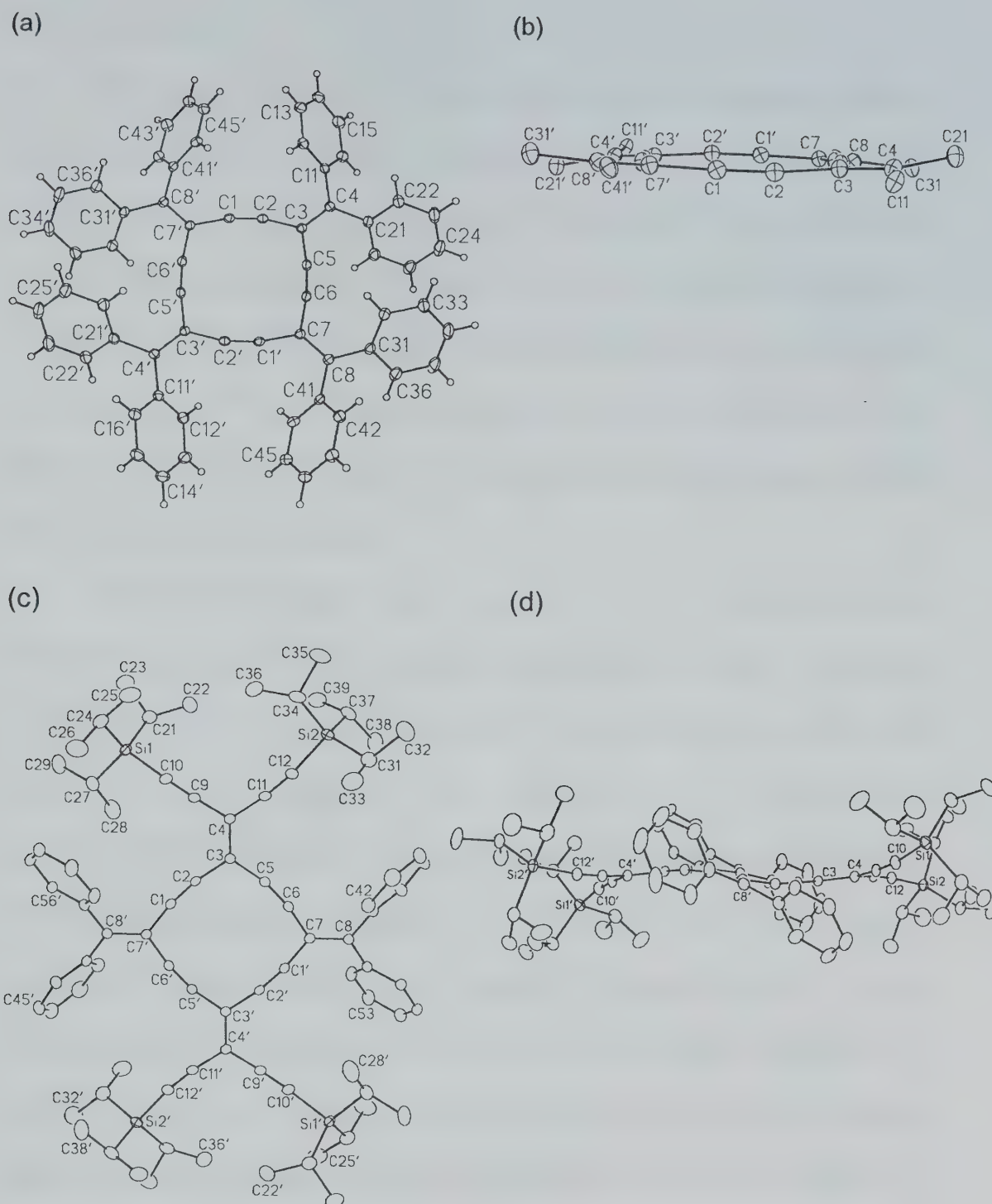


Figure 3-27 ORTEP drawings of [4]ERs (a) **2.63** top view, (b) **2.63** side view (only ipso carbons of pendent phenyl rings shown for clarity), (c) **2.64** top view, and (d) **2.64** side view (all at 20% probability level; hydrogen atoms not shown in c and d for clarity).

3.4 Conclusions

The work covered in this chapter has clearly demonstrated that it is possible to tune the properties of the *iso*-PDAs and **[4]ERs** via the incorporation of donor and/or acceptor substituents. Important for the study of these compounds is the fact that both *iso*-PDAs and **[4]ERs** of molecules demonstrate reasonable environmental and thermal stability. A combination of ^{13}C NMR spectroscopy and HR ESI or MALDI mass spectrometry have been crucial for the unequivocal identification of these highly symmetrical structures.

Salient trends have been identified from the analyses of the electrochemical, UV-Vis and fluorescence spectroscopic data. In general, a red-shift of the lowest-energy λ_{max} and λ_{em} occurs upon cyclization of *iso*-PDAs to form **[4]ERs**. It has been found that donor-acceptor substitution of the radialene skeleton leads to a bathochromic shift of the lowest energy λ_{max} in comparison to either the donor- or acceptor-substituted **[4]ERs** alone. This conclusion is supported by UV-Vis spectroscopic and CV data. Furthermore, electrochemical studies have shown that the energy levels of the HOMO and LUMO of the D-A **[4]ERs** resemble those of their individual components i.e. the corresponding *iso*-PDAs. On the contrary, UV-Vis spectroscopic analysis revealed that the electronic absorption properties of D-A substituted systems do not mirror that of their constituent parts, i.e. the corresponding *iso*-PDAs, but display new features, which suggest that macrocyclic cross-conjugation effects

may be at play. In general, it has been found that strongly-electron donating groups enhance emission properties versus electron-withdrawing groups. Furthermore, the presence of donors *and* acceptors on [4]ER skeleton results in fluorescence quenching. Additionally, it has been found that the observed Stokes shift decreases upon cyclization, consistent with the more constrained conformation of the radialene framework. In one case, X-Ray crystallography has been shown that the acetylene units of the cyclic core adopt bond angles similar to that of the other [4]ERs known to the group.^{2b-c} It is clear that further studies, such as theoretical calculations, are needed to ascertain and confirm the findings of this work, particularly with respect to electronic structure.

3.5 References and notes

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(5) In all cases, for emission spectra reported in this chapter, the following conditions apply. Quantum yields were not measured. For each sample in a given comparison, emission was measured under identical conditions and the concentration of each solution was adjusted so that the absorbance is below 0.05 absorbance units as measured for the most intense absorption in the UV-Vis spectrum.

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- (11) Torsion angles were calculated from the angle between the least squares plane generated from the 12 carbon atoms that define the cyclic radialene core and the six carbon and one nitrogen atoms that define the anilino residues.

Chapter 4 Conclusions and future directions

The work presented in this Thesis revolves around two central themes: (1) the development of a modular approach to synthesize 2D-conjugated push-pull molecules, and (2) the elucidation of structure-property relationships with respect to donor-acceptor substitution which can be used as predictive tools to optimize third-order NLO responses. While the study of the NLO characteristics of these molecules has not yet been accomplished, several salient points emerge from the work described in this Thesis. First, a new vinyl triflate building block has been synthesized that greatly expands a previous protocol developed in the Tykwinski laboratory through the incorporation of strong electron-donating groups (i.e., diisopropylanilino groups). A sequence of deprotection and Sonogashira cross-coupling reactions between vinyl triflates and terminal ene-diynes has been used to assemble *iso*-PDAs with a wide-range of functionalities. A complementary approach, which relied on the use of orthogonal alkyne-protecting groups, has been developed for the incorporation of electron-withdrawing functionalities.

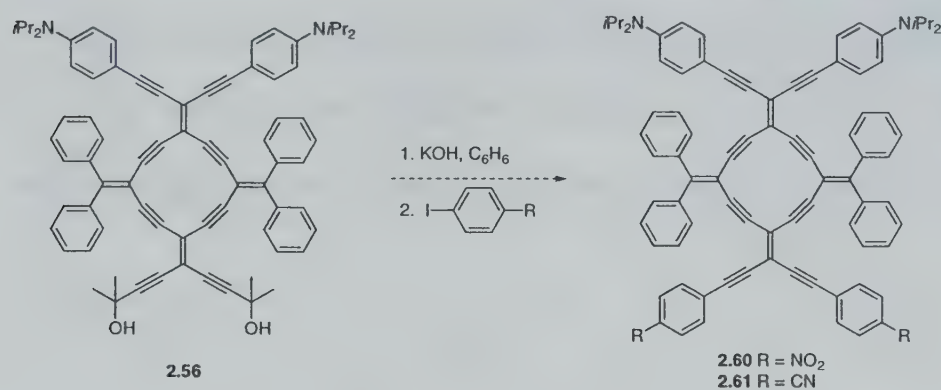
The *iso*-PDAs demonstrate reasonable thermal and shelf stabilities, and they are typically soluble in common organic solvents. As a result, common purification techniques such as FCC and recrystallization are usually applicable. Furthermore, solubility and stability, in turn, also facilitate characterization using NMR, UV-Vis and fluorescence spectroscopies as well as cyclic voltammetry. Precursor **[4]ERs** were

synthesized via a generalized protocol involving a sequence of deprotection and Sonogashira cross-coupling reactions between *iso*-PDAs and dibromoolefins. Further functionalization of the **[4]ER** framework with donors/acceptors was achieved via deprotection and subsequent two-fold Sonogashira cross-coupling reactions between the terminal alkynes and various aryl iodides. The **[4]ERs** exhibit surprising thermal and environmental stabilities, as well as good solubility in common solvents (e.g., CH₂Cl₂, CHCl₃, and THF). The latter property greatly facilitates the isolation, purification, and characterization of these carbon-rich molecules.

The electrochemical, electronic absorption and emission properties of the *iso*-PDAs and **[4]ERs** vary distinctly based on the results of cyclic voltammetry UV-Vis and fluorescence spectroscopic investigations. Strongly electron-donating groups increase emission more than electron-withdrawing groups for both *iso*-PDAs and **[4]ERs**. Moreover, the wavelength of maximum emission shifts to lower energy upon donor-substitution versus acceptor-substitution. Thus, it is clear that the *N,N*-diisopropylanilino groups play a crucial role in not only the enhancement of solubility and stability of the carbon-rich, electron-deficient π -conjugated frameworks, but also modulate their electronic and optical properties. Additionally, D-A substitution of the **[4]ER** affords a smaller band gap as compared to donor or acceptor substitution only. This observation is in line with the findings of Diederich and coworkers, who propose that smaller band gaps are observed when donor and acceptor are separated by an

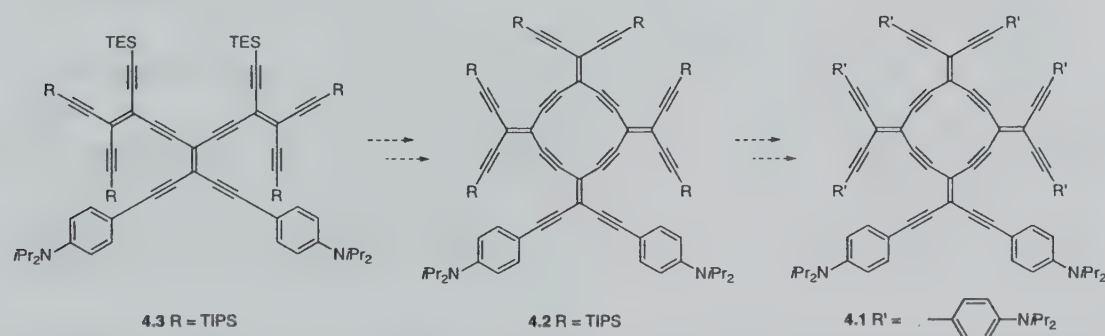
extended π -spacer (i.e. the **[4]ER** framework). This is because the energy levels of the HOMO and LUMO resemble those of the constituent parts.^{3e} The X-Ray crystal structure of **2.52** reveals that the radialene framework is not particularly strained, and in the solid state it maintains a planar structure conducive to effective π -overlap within the conjugated framework, comparable to other **[4]ERs** known to the Tykwinski group.¹ Thus, the electrochemical, UV-Vis, fluorescence, and X-Ray crystallographic data suggest that electronic communication is possible between the electron-donating or -withdrawing group and the macrocyclic core. One can also tentatively conclude from these data that the 2D-conjugated framework of the **[4]ER** facilitates communication between the electron-donating and withdrawing functionalities via cross-conjugation. Additional studies are, however, still required. This would include a computation/experimental analysis of bond length alternation and the extent of quinoid character of aromatic rings. Furthermore, theoretical calculations are needed to shed light on the exact location of the HOMO and LUMO for these novel molecules, which would help confirm the presence of the predicted charge-transfer interactions.^{3e} Experimentally, solvatochromism in both the electronic absorption and emission spectra of both D-A *iso*-PDA precursors and radialenes should be explored to complement theoretical studies of intramolecular charge-transfer interactions.

The future holds many possibilities for the extension of this research project. Firstly, an alternative route to the D-A substituted [4]ERs **2.60** and **2.61** from **2.56** is eminently close (Scheme 4-1), and should be compared in terms of efficiency to the route described in Chapter 2.



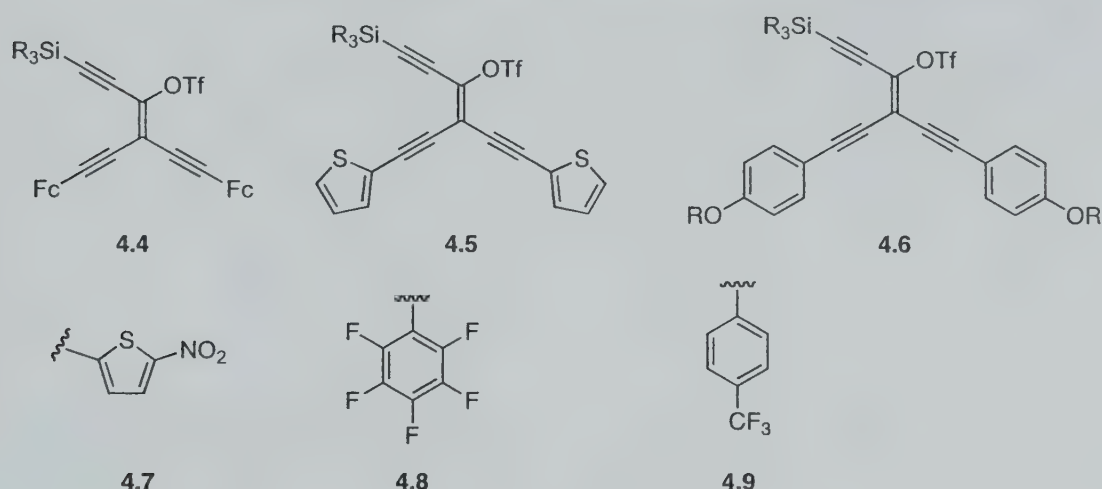
Scheme 4-1 Alternative route to D-A [4]ERs **2.60** and **2.61**

Furthermore, all-donor substituted [4]ER **4.1** (Scheme 4-2) is also of interest based on the results of the work in this thesis and of others.^{2,3} Compound **4.1** is envisioned to come from **4.2** which can be assembled from the corresponding *iso*-PDA **4.3** and the TIPS-dibromoolefin. Clearly, however, the necessary six-fold Sonogashira reaction from **4.2** to **4.1** will likely be a challenge.

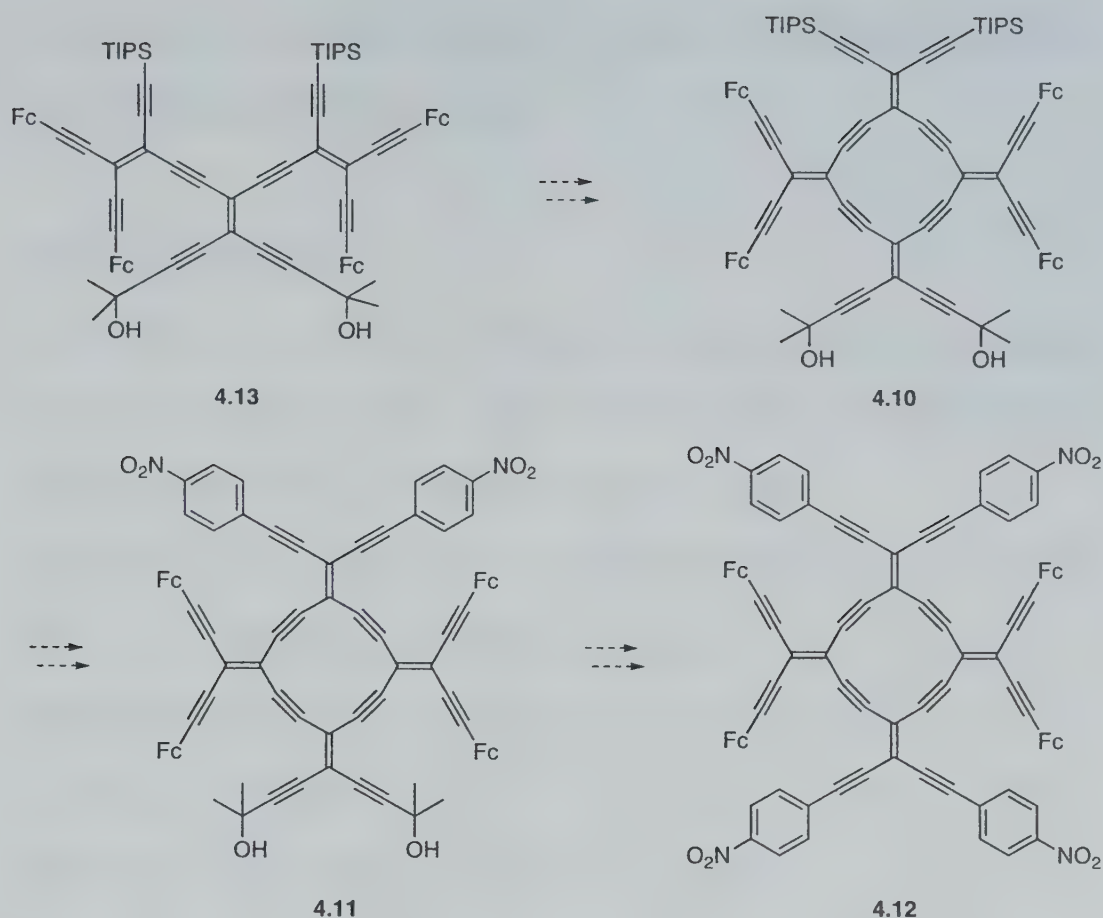


Scheme 4-2 Proposed synthesis of donor-substituted [4]ERs **4.1** and **4.2** from **4.3**

Vinyl triflates that can be incorporated into the synthetic design of *iso*-PDAs and [4]ERs and have precedent in the Tykwinski group include the ethynyl-ferrocenyl (**4.4**), ethynyl-thiophene (**4.5**), and ethynyl-alkoxy aryl donors (**4.6**).⁴ Other acceptors which can potentially give rise to molecules with interesting properties include when integrated into D-A systems include the nitrothienyl group (**4.7**)⁵ and the inductively-withdrawing pentafluorophenyl (**4.8**)^{2e} and benzotrifluoride (**4.9**) groups.^{2e}



The series of D-A [4]ERs **4.10-4.12** is alluring based on the ethynyl-ferrocenyl vinyl triflate, as shown in Scheme 4-3. They are envisioned to derive from **4.13**, which has been synthesized and characterized spectroscopically. Radialenes **4.10-4.12** are predicted to have interesting and desirable electrochemical properties, not only due to the presence of the donor-acceptor interactions, but also because of the redox-active ferrocene moieties.⁶



Scheme 4-3 Proposed synthesis of ferrocenyl-substituted **[4]ERs 4.10-4.12**

In conclusion, a viable synthetic route has been developed and used to gain access the first examples of D-A substituted **[4]ERs**. It is clear there is still a lot of room for the expansion of the current series of D-A substituted **[4]ERs** in order to provide a better understanding of the electronic-make-up and communication that exists in these novel cross-conjugated compounds. This can be achieved through a variation of symmetry as well as the strength of donors/acceptors, and conjugation paths. Additionally, this will aid in the establishment of additional structure-property relationships which can then be used as predictive tools to “tune”

the properties of the [4]ER to provide molecules that can later be studied for their third-order NLO responses.

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Chapter 5 Experimental section

General experimental

Reagents were purchased in reagent grade from commercial suppliers and used without further purification. Functionalized aryl acetylenes were prepared via Sonogashira cross-coupling of the corresponding aryl halide and trimethylsilylacetylene followed by protodesilylation using K_2CO_3 in MeOH (ca. 1:5). THF and Et_2O were distilled from sodium benzophenone ketyl. Anhydrous $MgSO_4$ was used as the drying agent after aqueous work-up. Filtration, evaporation and concentration in vacuo were done at water aspirator pressure. All reactions were performed in standard, dry glassware under an inert atmosphere of argon. Column chromatography: silica gel (230–400 mesh). Thin layer chromatography (TLC): pre-coated plastic sheets covered with 0.20 mm silica gel with fluorescent indicator UV 254 nm; visualization by UV light or $KMnO_4$ stain. Melting points are uncorrected. 1H - and ^{13}C NMR spectra are collected at 27 °C in $CDCl_3$, CD_2Cl_2 , $THF-d_8$ and $(CD_3)_2CO$; solvent peaks as reference. Coupling constants are reported as observed (± 0.5 Hz). For simplicity, the coupling constants of the aryl protons for *para*-substituted aryl groups have been reported as pseudo first-order (i.e. doublets), even though they are second-order ($AA'XX'$) spin systems.

UV-Vis spectra were acquired at rt using a Varian Cary 400 Scan spectrometer; λ_{max} in nm (ϵ in $M^{-1}cm^{-1}$). The λ_{max} of shoulder absorptions

are approximated to be Gaussian curves and the value of both the absorption and molar absorptivity were estimated based on this approximation. Emission spectra were recorded using Photon Technology International (PTI) MPI Fluorescence system.

For mass spectral analyses, low- and high-resolution data are provided in cases when M^+ was not the base peak. Otherwise, only high-resolution data are provided. The samples for ESI mass spectrometry were dissolved in CH_2Cl_2 and made use of a 3:1 MeOH/toluene mixture as the carrier solvent. MALDI mass spectrometry used the matrix *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB).

Differential scanning calorimetry (DSC) measurements were carried out on a Perkin Elmer Pyris 1 DSC instrument. All thermal analyses were carried out on under a flow of nitrogen with a heating rate of 10 °C/min. Melting points from DSC analysis are reported as the peak maxima, except in cases when the sample decomposed, in which case the onset temperature of the decomposition exothermic peak is reported, as well as the exothermic maxima corresponding to the decomposition.

Cyclic voltammetry experiments were conducted in deoxygenated CH_2Cl_2 on a Pt working electrode with a Ag/Ag⁺ pseudoreference (0.01 M AgNO₃, 0.1 M Bu₄NPF₆ in CH₃CN), and a Pt coil as counter electrode. Fc⁺/Fc was used as an internal reference. Peak potential, E° , for *irreversible* waves are estimated as $E^\circ = (E_{peak} + E_{onset})/2$ while that of

reversible and quasi-reversible waves is calculated as $(E_{pa} + E_{pc})/2$. Using a scan rate of 150 mV, waves that possess peak widths similar to that of the Fc/Fc^+ , i.e. 90–100 mV, and whose peak heights have a ratio of 1:1, have been designated reversible. If, however, the ratio of peak heights is 1:1, *but* peak widths are greater than that of Fc/Fc^+ (90–100 mV), then the waves are designated quasi-reversible. The electrochemical HOMO-LUMO gap is taken as the absolute value of $(E_{ox1} - E_{red1})$.

General Procedure A – Alcohol formation via lithium acetylide.

Unless otherwise noted in the individual procedures, a solution of the appropriate terminal acetylene (35.6 mmol) in THF (200 mL) was cooled to 0 °C. HexLi (35.4 mmol, 2.3 M in hexanes) was added slowly over 5-10 minutes and the mixture allowed to stir for 30 minutes. Ethyl formate (1.25 mL, 15.5 mmol) was dissolved in THF (ca. 5 mL), and then added slowly to the lithium acetylide solution over a period of 5-10 minutes. The reaction was allowed to stir for 30-45 minutes and then quenched with satd. aq. NH_4Cl (50 mL). Et_2O (100 mL) was then added, the organic layer separated, washed successively with satd. aq. NH_4Cl (2 x 50 mL), H_2O (2 x 50 mL), brine (2 x 50 mL), dried ($MgSO_4$), filtered, and the solvent removed in vacuo. Column chromatography (silica gel), if necessary, provided the pure alcohol.

General Procedure B – PCC oxidation of alcohol to ketone.

Unless otherwise noted in the individual procedures, to a solution of alcohol (14.3 mmol) in CH_2Cl_2 (200 mL) at rt were added PCC (24.3

mmol), celite (7 g), and molecular sieves (4 Å, 7 g). TLC analysis was used to monitor the reaction, and oxidation to the ketone was typically complete after 8 h. The reaction mixture was passed through a plug of silica gel (CH_2Cl_2) to remove chromium waste and the solvent removed in vacuo. Column chromatography (silica gel), if necessary, provided the pure ketone.

General Procedure C – Dibromoolefination. Unless otherwise noted in the individual procedures, CBr_4 (17.6 mmol) and PPh_3 (35.3 mmol) were added to CH_2Cl_2 (200 mL) and allowed to stir for 30-45 minutes at rt until the mixture turned bright orange. The ketone (13.6 mmol) in CH_2Cl_2 (50 mL) was slowly added to the $\text{CBr}_4/\text{PPh}_3$ mixture over a period of 10 min. The reaction turned darker red/orange color upon the addition of the ketone. TLC analysis was used to monitor the reaction, and oxidation to the ketone was typically complete after 3-6 h. The solvent was reduced to ca. 5 mL, hexanes added (100 mL), the inhomogeneous mixture filtered through a plug of silica gel (hexanes), and the solvent removed in vacuo. Column chromatography (silica gel), if necessary, provided the pure dibromoolefin.

General Procedure D – Tetraethynylethene (TEE) formation. Unless otherwise noted in the individual procedures, the terminal acetylene (10.4 mmol) was added to a degassed and dry solution of the dibromoolefin (2.61 mmol) and $i\text{Pr}_2\text{NH}$ or Et_3N (50 mL) in THF. $\text{PdCl}_2(\text{PPh}_3)_2$ (0.13 mmol) or $\text{Pd}(\text{PPh}_3)_4$ (0.13 mmol) and CuI (0.26 mmol)

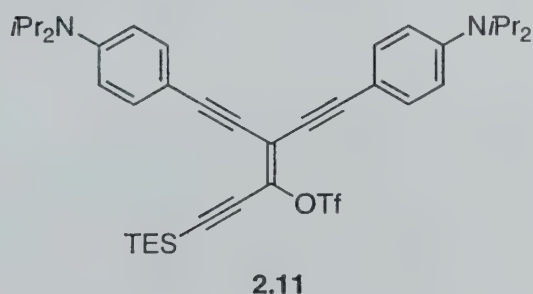
were added sequentially and the solution stirred at rt until TLC analysis showed the absence of the dibromoolefinic starting material (ca. 2-3 d). Et₂O (10 mL) and NH₄Cl (25 mL) were added, the organic phase separated, washed successively with sat'd aq. NH₄Cl (2 x 50 mL), H₂O (2 x 50 mL), brine (2 x 50 mL), dried (MgSO₄), filtered, and the solvent removed in vacuo. Column chromatography (silica gel) yielded the desired TEE.

General Procedure E – *Iso*-PDA formation. Unless otherwise noted in the individual procedures, a mixture of the appropriate trimethylsilyl- or triisopropylsilyl enyne and K₂CO₃ (ca. 1 equiv) or TBAF (2.2 equiv) in wet THF/MeOH (1:4, 25 mL) or THF (25 mL), respectively, was stirred under the conditions described in the individual procedures until the starting material was no longer visible by TLC analysis. Et₂O (10 mL) and satd. aq. NH₄Cl (5 mL) were added and the organic phase separated, washed successively with satd. aq. NH₄Cl (2 x 50 mL), H₂O (2 x 50 mL), brine (2 x 50 mL), dried (MgSO₄), filtered, reduced to ca. 2 mL, and added to a degassed solution of the vinyl triflate (1 equiv per coupling event) in THF (20 mL). Pd(PPh₃)₄ or PdCl₂(PPh₃)₂ (ca. 0.05 equiv), and *i*Pr₂NH or Et₃N (ca. 4 mL), and CuI (ca. 0.10 equiv) were sequentially added, and the solution stirred under conditions described in the individual procedures, until TLC analysis no longer showed the presence of the desilylated enyne (ca. 24 h). Et₂O and H₂O were added, the organic phase separated, washed with satd. aq. NH₄Cl (2 x 50 mL), H-

Et_2O (2 x 50 mL), brine (2 x 50 mL), dried (MgSO_4), filtered, and the solvent removed in vacuo. Flash column chromatography and/or precipitation from CH_2Cl_2 by the addition of Et_2O , hexanes, or washing with MeOH provided the desired enyne oligomer.

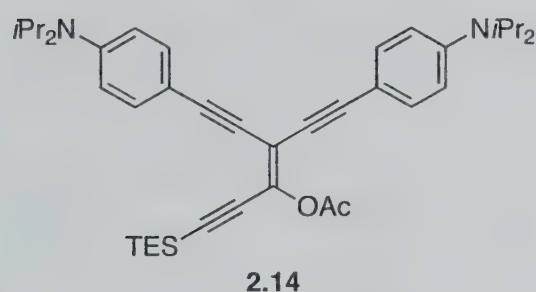
General Procedure F – Radialene formation. Unless otherwise noted in the individual procedures, a mixture of the appropriate *tert*butyldimethylsilyl or triethylsilyl *iso*-PDA and TBAF (2.2 equiv) in wet THF (10 mL) was stirred under the conditions described in the individual procedures until the starting material was no longer visible by TLC analysis. Et_2O (10 mL) and satd. aq. NH_4Cl (5 mL) were added and the organic phase separated, washed successively with satd. aq. NH_4Cl (2 x 50 mL), H_2O (2 x 50 mL), brine (2 x 50 mL), dried (MgSO_4), filtered, reduced to ca. 2 mL, and added to a degassed solution of the dibromoolefin in THF (20 mL). $\text{Pd}(\text{PPh}_3)_4$ or $\text{PdCl}_2(\text{PPh}_3)_2$ (ca. 0.05 equiv), *i* Pr_2NH or Et_3N , and CuI (ca. 0.10 equiv) were sequentially added and the solution refluxed until TLC analysis no longer indicated the presence of the deprotected *iso*-PDA (ca. 15-24 h). CH_2Cl_2 (10 mL) and satd. aq. NH_4Cl (5 mL) were added, the organic phase separated, washed successively with satd. aq. NH_4Cl (2 x 50 mL), H_2O (2 x 50 mL), brine (2 x 50 mL), dried (MgSO_4), filtered, and the solvent removed in vacuo. Flash column chromatography and/or precipitation from CH_2Cl_2 by the addition of Et_2O , hexanes, or washing with MeOH provided the desired radialene.

General Procedure G – Radialene functionalization. To a solution of the appropriate triisopropylsilyl-susbstituted **[4]ER** wet THF (10 mL) at 0 °C was added TBAF (2.2 equiv) and the solution stirred until the starting material was no longer visible by TLC analysis (ca. 5-10 min). Et₂O (5 mL) and satd. aq. NH₄Cl (2 mL) were added at 0 °C and the organic phase separated, washed successively with satd. aq. NH₄Cl (2 x 50 mL), H₂O (2 x 50 mL), brine (2 x 50 mL), dried (MgSO₄), filtered, reduced to ca. 2 mL, and added to a degassed solution of the TIPS-dibromoolefin **2.22** in THF (2 mL). Pd(PPh₃)₄ (ca. 0.05 equiv), *i*Pr₂NH (0.5 mL), and CuI (ca. 0.1 equiv) were added sequentially and the solution stirred under conditions described in the individual procedures until TLC analysis no longer showed the presence of the deprotected radialene (ca. 15-18 h). Et₂O (5 mL) and satd. aq. NH₄Cl (2 mL) were added, the organic phase separated, washed successively with satd. aq. NH₄Cl (2 x 25 mL), H₂O (2 x 25 mL), brine (2 x 25 mL), dried (MgSO₄), filtered, and the solvent removed in vacuo. FCC and/or precipitation/washing with Et₂O, hexanes or MeOH provided the functionalized **[4]ER**.



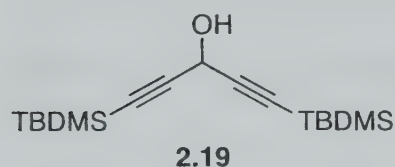
Vinyl acetate **2.14** (0.50 g, 0.80 mmol) was dissolved in THF (5 mL) and the solution cooled to –78 °C. To this solution was added MeLi (1.0

mL, 1.6 mmol, 1.6 M in Et₂O). The mixture was then stirred at –78 °C for 1 h. To this mixture was then added Tf₂O (0.45 g, 0.27 mL, 1.6 mmol) and the reaction mixture allowed to stir at –78 °C until TLC analysis no longer indicated the presence of **2.14**. Et₂O (15 mL) and satd. aq. NH₄Cl (10 mL) were added, the organic phase separated, washed successively with satd. aq. NH₄Cl (2 x 50 mL), H₂O (2 x 50 mL), brine (2 x 50 mL), dried (MgSO₄), filtered, and the solvent removed in vacuo. Silica gel filtration (EtOAc/hexanes 1:40) as eluent provided the crude vinyl triflate **2.11** in nearly quantitative yield as a dark yellow oil and was carried on to the subsequent step without further purification. *R*_f = 0.30 (EtOAc/hexanes 1:9). ¹H NMR (400 MHz, (CD₃)₂CO) δ 7.37-7.33 (m, 4H), 6.88-6.86 (m, 4H), 3.87 (septet, *J* = 6.8 Hz), 1.31-1.29 (m, 24H), 1.06 (t, *J* = 7.9 Hz, 9H), 0.94 (q, *J* = 7.9 Hz, 6H). ESI MS *m/z* 713.3 ([*M* + *H*]⁺, 100); ESI HRMS calcd. for C₃₉H₅₂N₂O₃F₃SiS (*M* + *H*)⁺ 713.3415, found 713.3414.



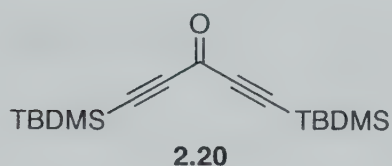
To a degassed solution of dibromovinyl acetate **2.12** (1.16 g, 3.04 mmol), **2.13** (1.65 g, 8.19 mmol), and *i*Pr₂NH (5 mL) in anhydrous THF (15 mL) was added sequentially PdCl₂(PPh₃)₂ (0.11 g, 0.15 mmol) and CuI (0.057 g, 0.30 mmol). The reaction mixture was allowed to stir at rt until TLC analysis no longer indicated the presence of **2.12** (ca. 1-2 d). Et₂O (5

mL) and satd. aq. NH_4Cl (5 mL) were added, the organic phase separated, washed successively with satd. aq. NH_4Cl (2 x 50 mL), H_2O (2 x 50 mL), brine (2 x 50 mL), dried (MgSO_4), filtered, and the solvent removed in vacuo. FCC (THF/hexanes 3:100 $\rightarrow$ 13:100) provided **2.14** (1.50 g, 79%). Mp 52-55 °C. R_f = 0.37 (THF/hexanes 3:17). IR (CH_2Cl_2 , cast) 2968, 2935, 2875, 2182, 2130, 1780, 1604, 1295 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.30 (d, J = 9.1 Hz, 2H), 7.25 (d, J = 9.1 Hz, 2H), 6.73 (m, 4H), 3.89-3.81 (m, 4H), 2.25 (s, 3H), 1.26 (d, J = 6.9 Hz, 24H), 1.01 (t, J = 7.9 Hz, 9H), 0.94 (q, J = 7.9 Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3 , APT) δ 167.4, 148.6, 148.5, 138.1, 132.43, 132.36, 115.7, 115.5, 109.7, 109.2, 106.9, 105.0, 100.7, 99.6, 96.6, 82.7, 81.8, 47.4, 21.11, 21.07, 20.7, 7.5, 4.2 (one signal coincident or not observed). ESI MS m/z 623.4 ($[\text{M} + \text{H}]^+$, 30), 312.2 ($[\text{M} + 2\text{H}]^{2+}$, 100); ESI HRMS calcd. for $\text{C}_{40}\text{H}_{55}\text{N}_2\text{O}_2\text{Si}$ ($\text{M}+\text{H}$) $^+$ 623.4027, found 623.4028. Anal. calcd. for $\text{C}_{40}\text{H}_{54}\text{N}_2\text{O}_2\text{Si}$: C, 77.12; H, 8.74; N, 4.50. Found: C, 77.21; H, 8.84; N, 4.59.

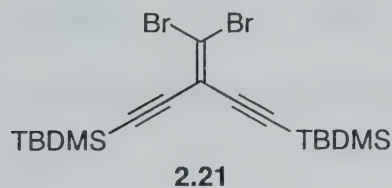


To a solution of TBDMS-acetylene (5.00 g, 6.66 mL, 35.6 mmol) in anhydrous THF was added HexLi (2.3 M in hexanes, 15.4 mL, 35.4 mmol) and ethylformate (1.15 g, 1.25 mL, 15.5 mmol) according to general procedure A to afford **2.19** (4.6 g, 96%) as a yellow oil. R_f = 0.27 (CH_2Cl_2 /hexanes 1:1). IR (CHCl_3 , cast) 3323 (br), 2953, 2929, 2886, 2858, 2177, 1250 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 5.05 (d, J = 7.7 Hz, 1H),

2.18 (m, 1H), 0.92 (s, 18H), 0.10 (s, 12H); ^{13}C NMR (125 MHz, CDCl_3 , APT) δ 102.6, 87.9, 53.0, 26.0, 16.6, -4.9 . EIMS m/z 308.2 (M^+ , 75), 73.0 ($[\text{SiMe}_3]^+$, 72). HRMS calcd. for $\text{C}_{17}\text{H}_{32}\text{OSi}_2$ (M^+) 308.1992, found 308.1993. Anal. calcd. for $\text{C}_{17}\text{H}_{32}\text{OSi}_2$: C, 66.16; H, 10.45. Found: C, 66.28; H, 10.48.

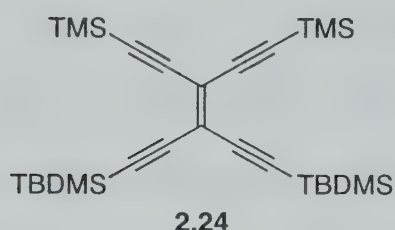


Alcohol **2.19** (4.41 g, 14.3 mmol) in CH_2Cl_2 was subjected to oxidation according to general procedure B using celite (7 g), molecular sieves (4 Å, 7 g) and PCC (5.24 g, 24.3 mmol) to afford **2.20** as a yellow oil (4.16 g, 95%). R_f = 0.58 (CH_2Cl_2 /hexanes 1:1). IR (CH_2Cl_2 , cast) 2955, 2932, 2888, 2860, 2160, 1638, 1253 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.95 (s, 18H), 0.17 (s, 12H); ^{13}C NMR (125 MHz, CDCl_3) δ 159.9, 103.5, 98.62, 98.61, 25.9, 16.7, -5.4 ; EIMS m/z 306.2 ($[\text{M}]^+$, 10), 250.1 ($[\text{M}^+ - t\text{Bu}]$, 20). HRMS calcd. for $\text{C}_{17}\text{H}_{30}\text{OSi}_2$ (M^+) 306.1835, found 306.1834. Anal. calcd. for $\text{C}_{17}\text{H}_{30}\text{OSi}_2$: C, 66.60; H, 9.86. Found: C, 66.96; H, 10.10.

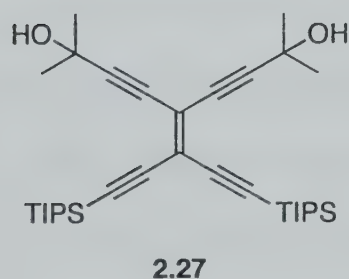


Ketone **2.20** (4.16 g, 13.57 mmol) was subjected to dibromoolefination according to the general procedure C using CBr_4 (5.85 g, 17.6 mmol) and PPh_3 (9.25 g, 35.3 mmol) in CH_2Cl_2 to afford **2.21** (5.86 g, 94%) as a yellow oil. R_f = 0.57 (hexanes). IR (CH_2Cl_2 , cast) 2954, 2930,

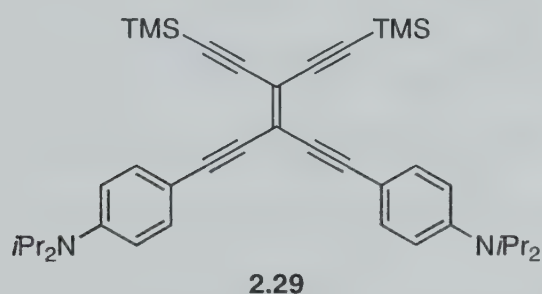
2886, 2858, 2155, 2132, 1471, 1251 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 0.95 (s, 18H), 0.14 (s, 12H); ^{13}C NMR (125 MHz, CDCl_3) δ 114.6, 109.8, 105.4, 101.2, 100.8, 26.1, 16.7, -5.0 . EIMS m/z 462.0 ($[\text{M}]^+$, 40), 73.0 ($[\text{SiMe}_3]^+$, 100); HRMS calcd. for $\text{C}_{18}\text{H}_{30}^{79}\text{Br}^{81}\text{BrSi}_2$ (M^+) 462.0232, found 462.0225. Anal. calcd. for $\text{C}_{18}\text{H}_{30}\text{Br}_2\text{Si}_2$: C, 46.75, H, 6.54. Found: C, 46.77, H, 6.54.



Dibromoolefin **2.21** (2.55 g, 5.54 mmol) and TMSA (2.18 g, 3.14 mL, 22.2 mmol) were subjected to TEE formation according to general procedure D to afford **2.24** (2.60 g, 95%) as a brown solid. Mp 147-150 $^{\circ}\text{C}$. R_f = 0.64 (hexanes). IR (CH_2Cl_2 , cast) 2954, 2898, 2859, 2162, 2144, 1254 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 0.94 (s, 18H), 0.19 (s, 18H), 0.13 (12H); ^{13}C NMR (125 MHz, CDCl_3 , APT) δ 118.8, 117.8, 105.2, 103.9, 101.9, 101.1, 26.1, 16.7, -0.3 , -4.8 . EIMS m/z 496.3 (M^+ , 59), 73.0 ($[\text{SiMe}_3]^+$, 100); HRMS calcd. for $\text{C}_{28}\text{H}_{48}\text{Si}_4$ (M^+) 496.2833, found 496.2830. Anal. calcd. for $\text{C}_{28}\text{H}_{48}\text{Si}_4$: C, 67.66, H, 9.73. Found: C, 67.33 H, 9.98.



TIPS-Dibromoolefin **2.22** (2.81 g, 5.14 mmol) and 2-methyl-3-butyn-2-ol (1.73 g, mL, 12.00 mL, 20.6 mmol) was subjected to TEE formation according to general procedure D to afford **2.27** (2.274 g, 80%) as a colorless solid. Mp 110-112 °C (discolors, decomp). R_f = 0.37 (EtOAc/hexanes 3:10); IR (CH₂Cl₂, cast) 3344 (br), 2944, 2866, 2208, 2146, 1240 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.02 (s, 2H), 1.55 (s, 12H), 1.10 (s, 42H); ¹³C NMR (125 MHz, CDCl₃, APT) δ 117.8, 116.0, 103.6, 102.7, 101.5, 79.7, 65.7, 31.1, 18.7, 11.2. ESI HRMS calcd. for C₃₄H₅₆NaO₂Si₂ ([M + Na]⁺) 575.37111, found 575.37136. Anal. calcd. for C₃₄H₅₆O₂Si₂: C, 73.85; H, 10.21. Found: C, 73.79; H, 10.24.



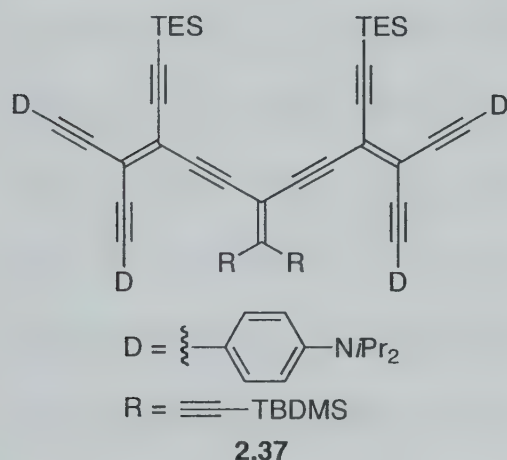
TMS-Dibromoolefin **2.23** (1.37 g, 3.62 mmol) and **2.13** (1.95 g, 22.2 mmol) was subjected to TEE formation according to general procedure D to afford **2.29** (1.20 g, 54%) as a an orange solid. Mp 165-167 °C. R_f = 0.44 (EtOAc/hexanes 1:9). IR (CH₂Cl₂, cast) 3088, 2969, 2934, 2198, 2171, 2136, 1603, 1518, 1295 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.33 (d, J = 8.8 Hz, 4H), 6.74 (d, J = 8.8 Hz, 4H), 3.86 (septet, J = 6.8 Hz, 4H), 1.28 (d, J = 6.8 Hz, 24H), 0.26 (s, 18H); ¹³C NMR (125 MHz, CDCl₃, APT) δ 148.7, 132.8, 121.3, 115.5, 111.8, 109.4, 103.0, 102.4, 101.1, 86.8, 47.4, 21.1, -0.01. EIMS m/z 618.4 (M⁺, 26), 73.0 ([SiMe₃]⁺, 76); HRMS calcd. for

C, 77.61; H, 8.79; N, 4.53. Found: C, 77.61; H, 9.01; N, 4.68.



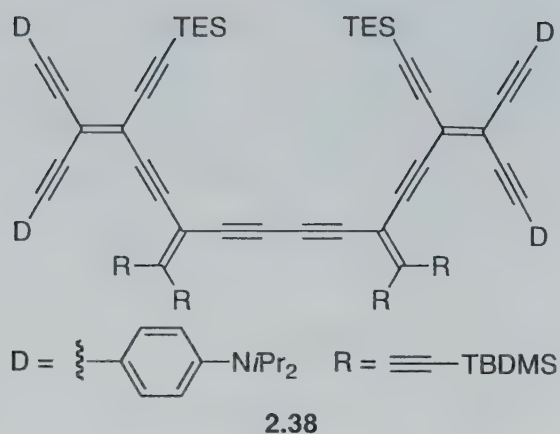
(0.059 g, 27%). Mp 144-147 °C R_f = 0.43 (EtOAc/hexanes 1:4). UV-vis (CH_2Cl_2) λ_{max} (ϵ) 465 (93 000), 318 (58 100), 288 (54 800) nm; IR (CH_2Cl_2 , cast) 2965, 2917, 2168, 2130, 1602, 1294 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.53-7.51 (m, 4H), 7.48 (d, J = 9.0 Hz, 4H), 7.32-7.24 (m, 10H), 6.74 (d, J = 9.1 Hz, 4H), 6.73 (d, J = 9.1 Hz, 4H), 3.88 (septet, J = 6.8 Hz,

4H), 3.81 (septet, $J = 6.8$ Hz, 4H), 1.29 (d, $J = 6.8$ Hz, 24H), 1.20 (d, $J = 6.8$ Hz, 24H), 1.12 (t, $J = 7.9$ Hz, 18H), 0.94 (q, $J = 7.9$ Hz, 12H); ^{13}C NMR (100 MHz, CDCl_3 , APT) δ 156.5, 148.6, 148.5, 140.2, 133.3, 132.6, 130.5, 128.3, 127.5, 119.9, 115.6, 115.5, 111.8, 109.9, 109.2, 103.0, 102.5, 102.1, 100.7, 100.2, 96.4, 90.8, 87.13, 87.09, 47.5, 47.4, 21.24, 21.21, 7.7, 4.6. HRMS MALDI m/z calcd. for $\text{C}_{94}\text{H}_{112}\text{N}_4\text{Si}_2$ (M^+) 1352.8420, found 1352.8414. DSC: Mp 144 °C, decomposition, 213 °C (onset), 240 °C (peak).

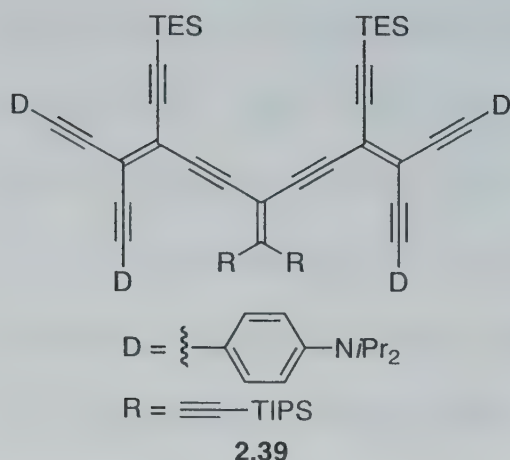


Compound **2.24** (0.065 g, 0.13 mmol) was desilylated via reaction with K_2CO_3 (0.018 g, 0.13 mmol) in THF/MeOH (12 mL, 1:5) and cross-coupled to vinyl triflate **2.11** (0.282 g, 0.396 mmol) in deoxygenated THF (5 mL) in the presence of $\text{PdCl}_2(\text{PPh}_3)_2$ (0.005 g, 0.007 mmol), $i\text{Pr}_2\text{NH}$ (4 mL), and CuI (0.002 g, 0.01 mmol) at 50-60 °C in a sealed flask for 18 h. The reaction mixture was allowed to cool to rt, Et_2O (35 mL) and satd. aq. NH_4Cl (25 mL) were added sequentially, the organic phase separated, washed successively with satd. aq. NH_4Cl (2 x 25 mL), H_2O (2 x 25 mL), brine (2 x 25 mL), dried (MgSO_4), filtered, and the solvent removed in

vacuo. FCC (silica gel, EtOAc/hexanes 1:40 $\rightarrow$ 1:3) provided the **2.37** in 51% (0.099 g, 51%). Mp 158-160 °C (discolors, decomp). R_f = 0.48 (EtOAc/hexanes 1:4). UV-vis (CH_2Cl_2) λ_{max} (ϵ) 547 (sh, 35 400), 471 (70 000), 300 (64 000) nm; IR (CH_2Cl_2 , cast) 3088, 2957, 2933, 2875, 2164, 2137, 1599, 1295 cm^{-1} ; ^1H NMR (500 MHz, CD_2Cl_2) δ 7.40 (d, J = 9.2 Hz, 4H), 7.33 (d, J = 9.2 Hz, 4H), 6.79 (d, J = 9.2 Hz, 4H), 6.76 (d, 9.2 Hz, 4H), 3.92 (septet, J = 6.9 Hz, 4H), 3.85 (septet, J = 6.9 Hz, 4H), 1.30 (d, J = 6.9 Hz, 24H), 1.23 (d, J = 6.9 Hz, 24H), 1.04 (t, J = 7.8 Hz, 18H), 0.97 (s, 18H), 0.71 (q, J = 7.8 Hz, 12H), 0.15 (s, 12H); ^{13}C NMR (125 MHz, CD_2Cl_2 , APT) δ 149.6, 149.5, 133.7, 133.2, 122.4, 118.0, 117.1, 115.61, 115.58, 110.6, 109.0, 108.6, 105.5, 104.1, 103.0, 102.7, 102.6, 101.8, 97.8, 94.3, 87.7, 87.5, 47.9, 47.8, 26.3, 21.2, 17.1, 7.8, 4.8, -4.7 (one signal coincident or not observed). ESI MS m/z 1479.0 ($[\text{M} + \text{H}]^+$, 10), 740.0 ($[\text{M} + 2\text{H}]^{2+}$, 100); ESI HRMS calcd. for $\text{C}_{98}\text{H}_{134}\text{N}_4\text{Si}_4$ ($[\text{M} + 2\text{H}]^{2+}$) 739.4837, found 739.4834 ($[\text{M} + 2\text{H}]^{2+}$). DSC: decomposition, 185 °C (onset), 224 (peak).

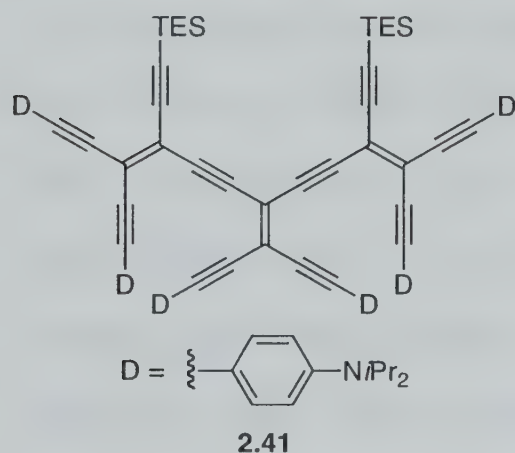


2.38 (0.036 g, 15%) was isolated during the purification of **2.37**. R_f = 0.50 (EtOAc/hexanes 1:4). IR (CH_2Cl_2 , cast) 2954, 2926, 2165, 2136, 1602, 1294 cm^{-1} ; ^1H NMR (500 MHz, CD_2Cl_2) δ 7.37 (d, J = 9.1 Hz, 4H), 7.34 (d, J = 9.1 Hz, 4H), 6.79 (d, J = 9.1 Hz, 4H), 6.73 (d, 9.1 Hz, 4H), 3.92 (septet, J = 6.9 Hz, 4H), 3.84 (septet, J = 6.9 Hz, 4H), 1.30 (d, J = 6.9 Hz, 24H), 1.24 (d, J = 6.9 Hz, 24H), 1.04 (t, J = 7.8 Hz, 18H), 0.98 (s, 18H), 0.94 (s, 18H), 0.72 (q, J = 7.8 Hz, 12 H), 0.18 (s, 12 H), 0.12 (s, 12H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 149.6, 149.5, 133.6, 133.2, 123.1, 120.2, 117.3, 115.6, 115.5, 110.0, 108.8, 108.3, 107.9, 106.9, 104.4, 102.9, 102.8, 102.2, 102.1, 101.8, 99.1, 93.1, 87.6, 83.7, 83.3 47.9, 26.3, 26.2, 21.2, 21.1, 17.02, 16.95, 7.7, 4.8, -4.7 , -4.8 (two signals coincident or not observed). HRMS MALDI m/z calcd. for $\text{C}_{120}\text{H}_{162}\text{N}_4\text{Si}_6$ (M^+) 1827.1410, found 1827.1400.



Compound **2.26** (0.114 g, 0.196 mmol) was desilylated via reaction with K_2CO_3 (0.0271 g, 0.196 mmol) in THF/MeOH (1:5) and cross-coupled to vinyl triflate **2.11** (0.429 g, 0.602 mmol) in deoxygenated THF (5 mL) in the presence of $\text{PdCl}_2(\text{PPh}_3)_2$ (0.007 g, 0.01 mmol), $i\text{Pr}_2\text{NH}$ (4 mL), and CuI (0.004 g, 0.02 mmol) at 50-60 °C in a sealed flask for 18 h. The reaction mixture was allowed to cool to rt, Et_2O (35 mL) and satd. aq. NH_4Cl (25 mL) were added sequentially, the organic phase separated, washed successively with satd. aq. NH_4Cl (2 x 25 mL), H_2O (2 x 25 mL), brine (2 x 25 mL), dried (MgSO_4), filtered, and the solvent removed in vacuo. FCC (silica gel, EtOAc/hexanes 1:40 $\rightarrow$ 1:3) provided the **2.39** (0.114 g, 37%). Mp 158-160 °C (discolors, decomp). R_f = 0.40 (EtOAc/hexanes 1:4). UV-vis (CH_2Cl_2) λ_{max} (ϵ) 538 (sh, 35 000), 468 (72 000), 302 (56 000) nm; IR (CH_2Cl_2 , cast) 2961, 2867, 2167, 2136, 1603, 1518, 1295 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.38 (d, J = 9.0 Hz, 4H), 7.31 (d, J = 9.0 Hz, 4H), 6.73 (d, J = 9.0 Hz, 4H), 6.71 (d, 9.0 Hz, 4H), 3.86 (septet, J = 7.0 Hz, 4H), 3.79 (septet, J = 7.0 Hz, 4H), 1.27 (d, J = 7.0 Hz, 24H), 1.19 (d, J = 7.0 Hz, 24H), 1.06 (s, 42H), 1.00 (t, J = 8.0 Hz, 18

H), 0.65 (q, $J = 8.0$ Hz, 12 H); ^{13}C NMR (125 MHz, CDCl_3 , APT) δ 148.8, 148.7, 133.3, 132.8, 121.7, 117.3, 117.1, 115.6, 111.3, 109.8, 109.3, 104.4, 103.2, 103.0, 102.9, 101.1, 100.8, 97.0, 94.2, 87.5, 87.3, 47.5, 47.4, 21.12, 21.10, 18.7, 11.3, 7.6, 4.5 (one signal coincident or not observed). ESI MS m/z 1563.1 ($[\text{M} + \text{H}]^+$, 15), 782.0 ($[\text{M} + 2\text{H}]^{2+}$, 100), 521.7 ($[\text{M} + 3\text{H}]^{3+}$, 45); ESI HRMS m/z calcd. for $\text{C}_{104}\text{H}_{146}\text{N}_4\text{Si}_4$ ($[\text{M} + 2\text{H}]^{2+}$) 781.5307, found 781.5310 ($[\text{M} + 2\text{H}]^{2+}$). DSC: decomposition, 205 °C (onset), 243 °C (peak).



Compound **2.29** (0.179 g, 0.289 mmol) was desilylated via reaction with K_2CO_3 (0.040 g, 0.29 mmol) in THF/MeOH (1:5) and cross-coupled to vinyl triflate **2.11** (0.713 g, 1.00 mmol) in deoxygenated THF (5 mL) in the presence of $\text{Pd}(\text{PPh}_3)_4$ (0.016 g, 0.014 mmol), $i\text{Pr}_2\text{NH}$ (4 mL), and CuI (0.006 g, 0.03 mmol) at rt in a sealed flask for 3 d. The reaction mixture was allowed to cool to rt, Et_2O (35 mL) and satd. aq. NH_4Cl (25 mL) were added sequentially, the organic phase separated, washed successively with satd. aq. NH_4Cl (2 x 25 mL), H_2O (2 x 25 mL), brine (2 x 25 mL), dried (MgSO_4), filtered and the solvent removed in vacuo. FCC (silica gel,

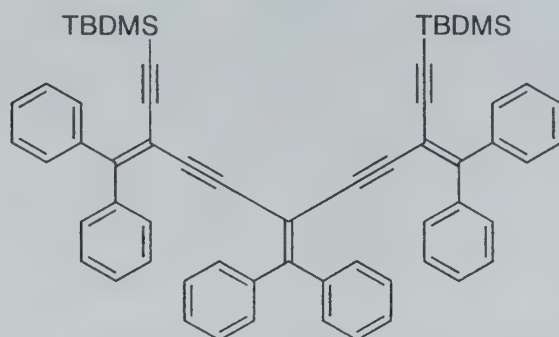
$D = \text{---} \text{C}_6\text{H}_4 \text{---} \text{N}i\text{Pr}_2$

 $R = \text{---} \text{C}_6\text{H}_5$

2.43

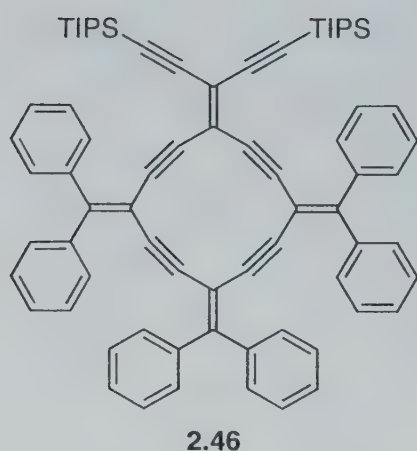
Compound **2.28** (0.0623 g, 0.123 mmol) was desilylated via reaction with TBAF (0.3 mL, 0.3 mmol, 1 M in THF) in wet THF (10 mL) and cross-coupled to vinyl triflate **2.11** (0.263 g, 0.369 mmol) in deoxygenated THF (5 mL) in the presence of Pd(PPh₃)₄ (0.007 g, 0.06 mmol), *i*Pr₂NH (4 mL), and CuI (0.002 g, 0.01 mmol) at 60 °C in a sealed flask overnight. The reaction mixture was allowed to cool to rt, Et₂O (35 mL) and satd. aq. NH₄Cl (25 mL) were added sequentially, the organic phase separated, washed successively with satd. aq. NH₄Cl (2 x 25 mL), H₂O (2 x 25 mL), brine (2 x 25 mL), dried (MgSO₄), filtered, and the solvent removed in vacuo. FCC (silica gel, EtOAc/hexanes 1:40 → 1:3) provided **2.43** (0.0472 g, 24%). Mp 125-128 °C (discolors, decomp). *R*_f = 0.36 (EtOAc/hexanes 1:4). UV-vis (CH₂Cl₂) λ_{max} (ε) 560 (sh, 42 500), 488 (70 000), 305 (76 000) nm; IR (CH₂Cl₂, cast) 2968, 2933, 2874, 2564, 2165, 1602, 1518, 1295 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.56-7.53 (m, 4H), 7.42 (d, *J* = 9.0 Hz, 4H), 7.33 (d, *J* = 9.0 Hz, 4H), 7.27-7.26 (m, 6H), 6.74 (d, *J* = 9.0 Hz, 4H), 6.67 (d, *J* = 9.0 Hz, 4H), 3.88 (septet, *J* = 7.0 Hz, 4H), 3.78 (septet, 7.0 Hz, 4H), 1.28 (d, *J* = 7.0 Hz, 24H), 1.18 (d, *J* = 7.0 Hz, 24H), 1.12 (t, *J* = 8.0 Hz, 18H), 0.94 (q, *J* = 8.0 Hz, 12H); ¹³C NMR (125 MHz, CDCl₃, APT) 148.84, 148.76, 133.4, 132.8, 132.3, 128.6, 128.1, 122.8, 121.3, 117.0, 116.6, 115.5, 115.4, 111.1, 109.6, 109.0, 103.8, 103.0, 101.8, 100.8, 99.8, 98.0, 95.1, 88.1, 87.5, 87.4, 47.4, 47.3, 21.11, 21.08, 7.5, 4.4. ESI MS *m/z* 1402.9 ([M + H]⁺, 65), 701.4 ([M +

$2\text{H}]^{2+}$, 100); ESI HRMS calcd. for $\text{C}_{98}\text{H}_{113}\text{N}_4\text{Si}_2$ ($[\text{M} + \text{H}]^+$) 1401.8498, found 1401.8488. DSC: decomposition, 159 °C (onset), 196 °C (peak).

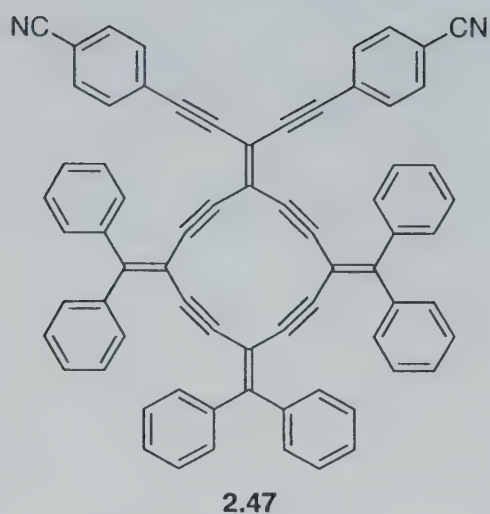


2.50

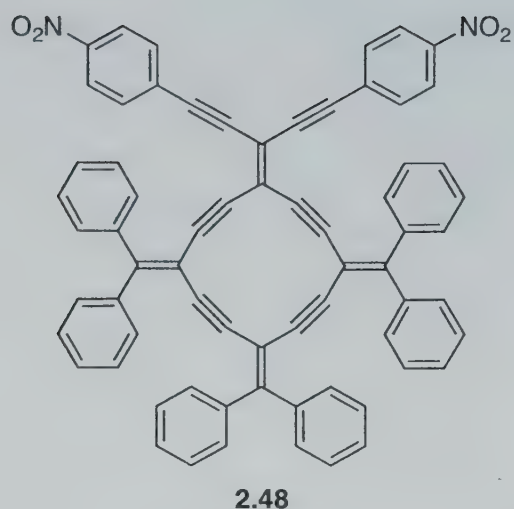
Synthesized as previously reported.¹ Compound **2.31** (0.470 g, 1.13 mmol) was desilylated TBAF (2.5 mL, 2.5 mmol, 1.0 M in THF) and cross-coupled to vinyl triflate **2.16** (1.06 g, 2.27 mmol) in deoxygenated THF (8 mL) in the presence of $\text{Pd}(\text{PPh}_3)_4$ (0.066 g, 0.57 mmol), $i\text{Pr}_2\text{NH}$ (2 mL) and CuI (0.021 g, 0.11 mmol) for 24 h at reflux according to general procedure E. FCC (silica gel, $\text{CH}_2\text{Cl}_2/\text{hexanes}$ 1:10 $\rightarrow$ 3:10) provided compound **2.50** (0.86 g, 89%) as a yellow foam. Mp 186 °C (DSC). R_f = 0.53 ($\text{CH}_2\text{Cl}_2/\text{hexanes}$ 3:7). UV-vis (CH_2Cl_2); λ_{max} (ϵ) 256 (50 500), 325 (27 300) 361 (31 600) nm; IR (CH_2Cl_2 , cast) 3081, 3055, 2954, 2928, 2144, 1493, 1249 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.46-7.24 (m, 30H), 0.88 (s, 18H), 0.10 (s, 12H); ^{13}C NMR (100 MHz, CDCl_3 , APT) δ 156.7, 154.9, 140.5, 140.0, 139.8, 130.4, 130.3, 130.2, 128.6, 128.2, 128.4, 128.2, 127.7, 127.6, 103.5, 102.1, 95.9, 90.6, 90.1, 26.1, 21.2, 16.7, -4.8. HRMS MALDI m/z calcd. for $\text{C}_{62}\text{H}_{60}\text{Si}_2$ (M^+) 860.4234, found 860.4222. DSC: mp = 186 °C.



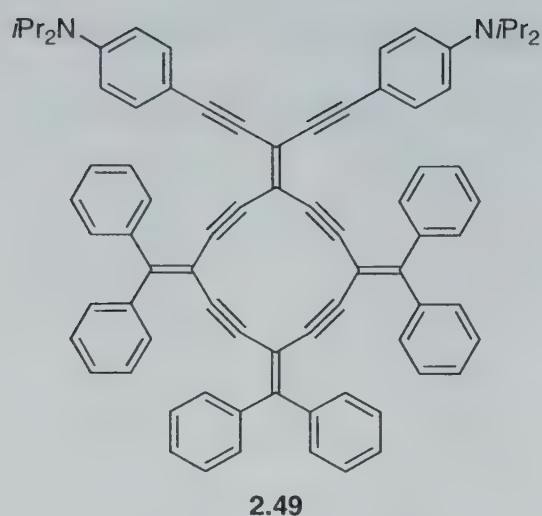
Iso-PDA **2.50** (0.505 g, 0.586 mmol) was desilylated using TBAF (1.3 mL, 1.3 mmol, 1.0 M in THF) and cross-coupled to dibromoolefin **2.22** (0.320g, 0.586 mmol) according to the general procedure F. FCC (silica gel, CH₂Cl₂/hexanes 1:10 → 3:10) and two-solvent recrystallization using CH₂Cl₂/hexanes at 5 °C provided **[4]ER 2.46** (0.22 g, 37%) as a yellow solid. Mp 273 °C (DSC). *R*_f = 0.32 (CH₂Cl₂/hexanes 1:1). UV-vis (CH₂Cl₂) λ_{max} (ε) 430 (sh, 29 100), 393 (94 900), 272 (37 000), nm; IR (CH₂Cl₂, cast) 3083, 3054, 2942, 2890, 2865, 2137; ¹H NMR (400 MHz, CDCl₃) δ 7.40-7.37 (m, 4H), 7.27-7.13 (m, 22H), 7.06-7.02 (m, 4H), 0.94-0.85 (m, 42H); ¹³C NMR (100 MHz, CDCl₃, APT) δ 151.8, 151.5, 140.0, 139.9, 139.8, 130.5, 130.2, 130.1, 128.9, 128.7, 128.5, 127.9, 127.8, 127.7, 117.6, 110.9, 104.0, 103.8, 102.6, 102.1, 102.0, 96.6, 96.5, 96.3, 18.5, 11.1. HRMS MALDI *m/z* calcd. for C₇₄H₇₂Si₂ (M⁺) 1016.5167, found 1016.5160. DSC: decomposition, 271 °C (onset), 303 °C (peak).



[4]ER 2.46 (0.025 g, 0.025 mmol) was desilylated using TBAF (0.1 mL, 0.01 mmol, 1.0 M in THF) and cross-coupled to 4-iodobenzonitrile (0.011 g, 0.050 mmol) in the presence of *i*Pr₂NH (2 mL), Pd(PPh₃)₄ (0.0014 g, 0.0012 mmol), and CuI (0.0006 g, 0.003 mmol) according to general procedure G. FCC (silica gel, CH₂Cl₂) and precipitation from CH₂Cl₂ by the addition of Et₂O afforded **[4]ER 2.47** as an orange solid (0.017 g, 76%). Mp 286-288 °C (discolors, decomp). *R*_f = 0.49 (CH₂Cl₂). UV-vis (CH₂Cl₂) λ_{max} (ε) 498 (sh, 13 200), 401 (76 800), 339 (52 300), 261 (48 000) nm; IR (CH₂Cl₂, cast) 3062, 2225, 2157, 1602 cm⁻¹; ¹H NMR (500 MHz, CD₂Cl₂) δ 7.56 (d, *J* = 8.6 Hz, 4H), 7.45-7.43 (m, 4H), 7.31-7.18 (m, 28H), 7.02-6.99 (m, 2H); ¹³C NMR (125 MHz, CD₂Cl₂) δ 154.0, 153.1, 140.12, 140.07, 139.7, 132.7, 132.3, 131.0, 130.4, 130.3, 129.7, 129.6, 129.3, 128.41, 128.39, 128.3, 127.0, 120.4, 118.7, 112.6, 108.9, 106.6, 102.2, 102.0, 97.3, 96.6, 96.4, 96.2, 90.1. HRMS MALDI *m/z* calcd. for C₇₀H₃₈N₂ (M⁺) 906.3030, found 906.3026. DSC: decomposition, 304 °C (onset), 319 °C (peak).

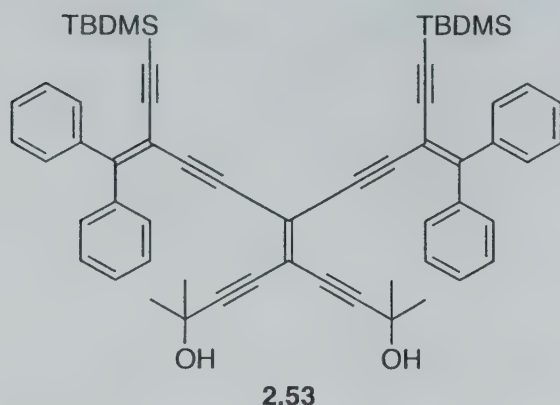


[4]ER 2.46 (0.027 g, 0.027 mmol) was desilylated using TBAF (0.1 mL, 0.1 mmol, 1.0 M in THF) and cross-coupled to 4-iodonitrobenzene (0.013 g, 0.054 mmol) in the presence of *i*Pr₂NH (2 mL), Pd(PPh₃)₄ (0.0016 g, 0.0014 mmol), and CuI (0.001 g, 0.003 mmol) according to general procedure G. FCC (silica gel, CH₂Cl₂) followed by precipitation from CH₂Cl₂ by the addition of Et₂O afforded **[4]ER 2.48** (0.024 g, 91%) as an orange solid. Mp 285 °C (discolors, decomp). *R*_f = 0.66 (CH₂Cl₂/hexanes 7:3). UV-vis (CH₂Cl₂) λ_{max} (ε) 497 (sh, 13 700), 402 (66 800), 264 (38 300) nm; IR (CH₂Cl₂, cast) 3099, 2924, 2853, 2167, 1342 cm⁻¹; ¹H NMR (500 MHz, CD₂Cl₂) δ 8.11 (d, *J* = 9.0 Hz, 4H), 7.47-7.45 (m, 4H), 7.31-7.13 (m, 28H), 7.03-7.00 (m, 2H); ¹³C NMR (125 MHz, CD₂Cl₂) δ 154.2, 153.2, 147.8, 140.15, 140.06, 139.7, 133.1, 131.0, 130.4, 130.3, 129.72, 129.70, 129.3, 129.0, 128.42, 128.40, 128.3, 123.8, 120.9, 108.6, 107.0, 102.2, 101.9, 97.4, 96.39, 96.38, 96.2, 90.9. HRMS MALDI *m/z* calcd. for C₆₈H₃₈N₂O₄ (M⁺) 946.2826, found 946.2821. DSC: decomposition, 297 °C (onset), 306 °C (peak).

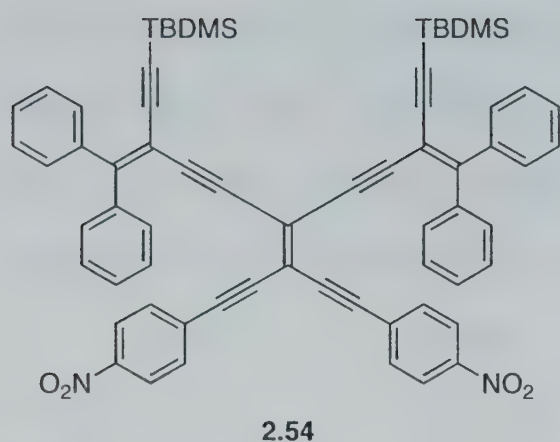


[4]ER 2.46 (0.025 g, 0.025 mmol) was desilylated using TBAF (0.1 mL, 0.01 mmol, 1.0 M in THF) and cross-coupled to 4-iodo-*N,N*-diisopropylaniline (0.015 g, 0.050 mmol) in the presence of *i*Pr₂NH (2 mL), Pd(PPh₃)₄ (0.0014 g, 0.0012 mmol), and CuI (0.001 g, 0.003 mmol) according to general procedure G. FCC (silica gel, 1:10 → 3:10 EtOAc/hexanes) followed by precipitation from CH₂Cl₂ by the addition of Et₂O afforded **[4]ER 2.49** (0.023 g, 88%) as a red solid. Mp 281 °C (discolors, decomp). *R*_f = 0.31 (EtOAc/hexanes 1:4). UV-vis (CH₂Cl₂) λ_{max} (ε) 542 (32 400), 495 (31 700), 401 (71 100), 280 (47 400) nm; IR (CH₂Cl₂, cast) 3082, 3053, 2969, 2928, 2170, 1603, 1295 cm⁻¹; ¹H NMR (500 MHz, CD₂Cl₂) δ 7.49-7.47 (m, 4H), 7.29-7.20 (m, 16H), 7.17-7.11 (m, 10H), 6.91 (d, *J* = 9.1 Hz, 4H), 6.68 (d, *J* = 9.1 Hz, 4H), 3.92 (septet, *J* = 6.9 Hz, 4H), 1.31 (d, *J* = 6.9 Hz, 24H); ¹³C NMR (125 MHz, CD₂Cl₂) δ 152.2, 151.8, 149.3, 140.3, 140.23, 140.19, 133.2, 130.9, 130.4, 130.3, 129.3, 129.14, 129.07, 128.30, 128.29, 128.25, 115.6, 113.4, 112.6, 108.6, 103.0, 102.6, 102.5, 101.3, 97.7, 97.0, 96.9, 86.7, 47.8, 21.2. HRMS MALDI *m/z* calcd.

for $C_{80}H_{66}N_2$ (M^+) 1054.5221, found 1054.5222. DSC: decomposition, 273 °C (onset), 285 °C (peak).

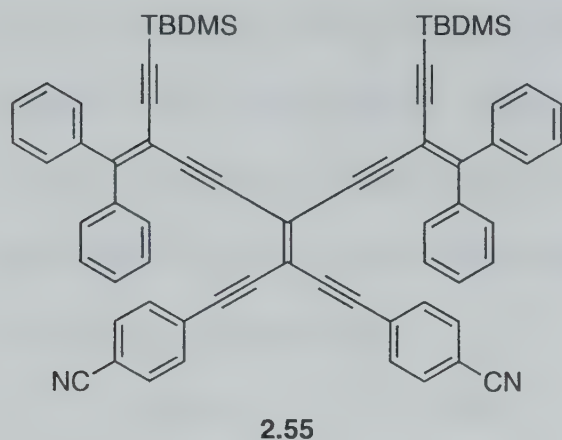


TEE **2.27** (0.31 g, 0.56 mmol) was desilylated using TBAF (1.2 mL, 1.2 mmol, 1.0 M in THF) and cross-coupled to vinyl triflate **2.16** (0.522 g, 1.12 mmol) in deoxygenated THF (5 mL) in the presence of $Pd(PPh_3)_4$ (0.032 g, 0.028 mmol), iPr_2NH (2mL), and CuI (0.011 g, 0.056 mmol) for 24 h at reflux according to general procedure E. FCC (silica gel, EtOAc/hexanes 1:5 $\rightarrow$ 1:1) provided compound **2.53** (0.42 g, 86%) as a yellow foam. Mp 59-63 °C. R_f = 0.43 (CH_2Cl_2 /hexanes 3:7). UV-vis (CH_2Cl_2) λ_{max} (ϵ) 395 (28 700), 319 (26 600), 255 (38 100) nm; IR (CH_2Cl_2 , microscope) 3566, 3373 (br), 3082, 3055, 2981, 2954, 2929, 2857, 2184, 2142, 1250 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$) δ 7.40-7.25 (m, 20H), 1.87 (s, 2H), 1.49 (s, 12H), 0.79 (s, 18H), 0.03 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$, APT) δ 158.6, 140.3, 139.6, 130.4, 130.3, 128.9, 128.5, 127.8, 127.7, 118.3, 115.2, 103.4, 103.0, 101.3, 97.1, 96.6, 88.2, 79.5, 65.5, 31.0, 26.0, 16.7, -4.8. ESI MS m/z HRMS calcd. for $C_{60}H_{64}O_2Si_2Na$ ($M + Na$) $^+$ 895.4337, found 895.4339. DSC: mp = 63 °C.



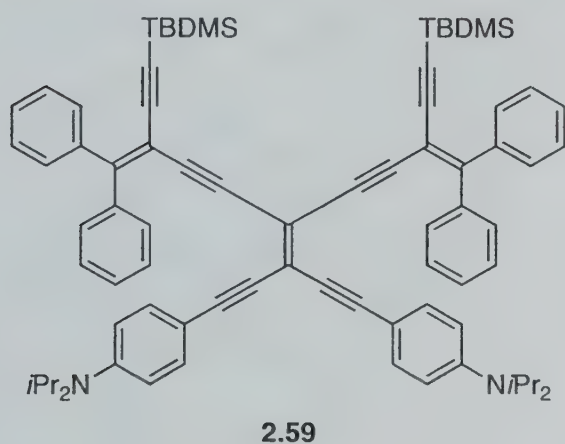
Is-PDA **2.53** (0.1032 g, 0.1182 mmol) was desilylated via reaction with KOH (0.010 g, 0.18 mmol) in C₆H₆ (10 mL) at reflux for 25 min. Aqueous work-up and silica gel filtration (CH₂Cl₂/hexanes 3:20) provided the crude terminal diyne (0.079 g, 88%) as a brown foam.² This product was cross-coupled to 4-iodonitrobenzene (0.050 g, 0.20 mmol) in deoxygenated THF (5 mL) in the presence of Pd(PPh₃)₄ (0.006 g, 0.005 mmol), *i*Pr₂NH (2 mL), and CuI (0.002 g, 0.01 mmol) at 40-50 °C for 18 h. The reaction was cooled to rt and Et₂O (10 mL) and H₂O (5 mL) were added, the organic phase separated, washed with satd. aq. NH₄Cl (2 x 50 mL), brine (2 x 50 mL), dried (MgSO₄), filtered, and the solvent removed in vacuo. FCC (silica gel, CH₂Cl₂ 1:1) followed by precipitation from hexanes afforded compound **2.54** (0.070 g, 70%) as an orange solid. Mp 161-162 °C. *R*_f = 0.47 (EtOAc/hexanes, 3:17). UV-vis (CH₂Cl₂) λ_{max} (ε) 460 (30 700), 321 (47 600), 249 (45 600) nm; IR (CH₂Cl₂, cast) 3055, 2953, 2928, 2175, 2144, 1341 cm⁻¹; ¹H NMR (400 MHz, CD₂Cl₂) δ 8.17 (d, *J* = 8.9 Hz, 4H), 7.58 (d, *J* = 8.9 Hz, 4H), 7.48-7.45 (m, 4H), 7.41-7.36 (m, 10H), 7.26-7.22 (m, 6H), 0.82 (s, 18H), 0.02 (s, 12H); ¹³C NMR (100 MHz, CD₂Cl₂)

δ 160.0, 147.8, 140.3, 139.8, 133.1, 130.75, 130.70, 129.6, 129.4, 129.1
128.20, 123.9, 120.4, 114.5, 103.1, 101.3, 100.4, 97.5, 96.9, 91.1, 90.2
88.6, 26.1, 16.9, -4.8. HRMS MALDI m/z calcd. for $C_{66}H_{58}N_2O_4Si_2$ (M^+),
998.3930 found 998.3930. DSC: mp = 164 °C.



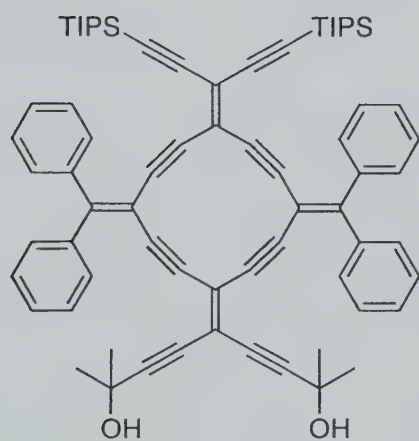
Iso-PDA **2.53** (0.146 g, 0.167 mmol) was desilylated via reaction with KOH (0.014 g, 0.25 mmol) in C_6H_6 (10 mL) at reflux for 25 min. Aqueous work-up and silica gel filtration (CH_2Cl_2 /hexanes 3:20) provided the crude terminal diyne (0.095 g, 75%) as a brown foam.² The product was cross-coupled to 4-iodobenzonitrile (0.060 g, 0.26 mmol) in deoxygenated THF (5 mL) in the presence of $Pd(PPh_3)_4$ (0.008 g, 0.007 mmol), iPr_2NH (2 mL), and CuI (0.0025 g, 0.013 mmol) at 40-50 °C for 18 h. The reaction was cooled to rt and Et_2O (10 mL) and H_2O (5 mL) were added, the organic phase separated, washed with satd. aq. NH_4Cl (2 x 50 mL), brine (2 x 50 mL), dried ($MgSO_4$), filtered, and the solvent removed in vacuo. FCC (silica gel CH_2Cl_2 /hexanes 3:10 $\rightarrow$ 1:1) followed by precipitation from hexanes afforded compound **2.55** (0.091 g, 76%) as a yellow solid. Mp 114-116 °C (discolors, decomp). R_f = 0.37

(EtOAc/hexanes 3:17). UV-vis (CH_2Cl_2) λ_{max} (ϵ) 448 (31 600), 332 (64 700), 251 (51 100) nm; IR (CH_2Cl_2 , cast) 3056, 2953, 2928, 2229, 2175, 2144, 1603 cm^{-1} ; ^1H NMR (500 MHz, CD_2Cl_2) δ 7.61 (d, J = 8.7 Hz, 4H), 7.50 (d, J = 8.7 Hz, 4H), 7.46-7.43 (m, 4H), 7.40-7.36 (m, 10H), 7.26-7.21 (m, 6H), 0.82 (s, 18H), 0.02 (s, 12H); ^{13}C -NMR (125 MHz, CD_2Cl_2) δ 160.0, 140.4, 139.9, 132.8, 132.5, 130.75, 130.69, 129.6, 129.3, 128.3, 128.2, 127.2, 119.8, 118.7, 114.8, 112.7, 103.2, 101.4, 100.0, 97.5, 97.2, 90.4, 88.6, 26.2, 16.9, -4.8. HRMS MALDI m/z calcd. for $\text{C}_{68}\text{H}_{58}\text{N}_2\text{Si}_2$ (M^+) 958.4133, found 958.4131.



Compound **2.29** (0.5466 g, 0.8830 mmol) was desilylated using K_2CO_3 (0.1220 g, 0.8830 mmol) and cross-coupled to vinyl triflate **2.16** (0.8240 g, 1.766 mmol) in deoxygenated THF (15 mL) in the presence of $\text{Pd}(\text{PPh}_3)_4$ (0.05 g, 0.04 mmol), $i\text{Pr}_2\text{NH}$ (2mL), and CuI (0.02 g, 0.09 mmol) according to general procedure E. FCC (silica gel, EtOAc/hexanes 3:10) provided compound **2.59** (0.74 g, 76%) as a red foam. Mp 160-163 $^\circ\text{C}$. R_f = 0.33 (EtOAc/hexanes 3:17). UV-vis (CH_2Cl_2) λ_{max} (ϵ) 475 (43 174), 388 (23 600), 318 (50 300) nm; IR (CH_2Cl_2 , cast) 3083, 3054, 2956, 2927,

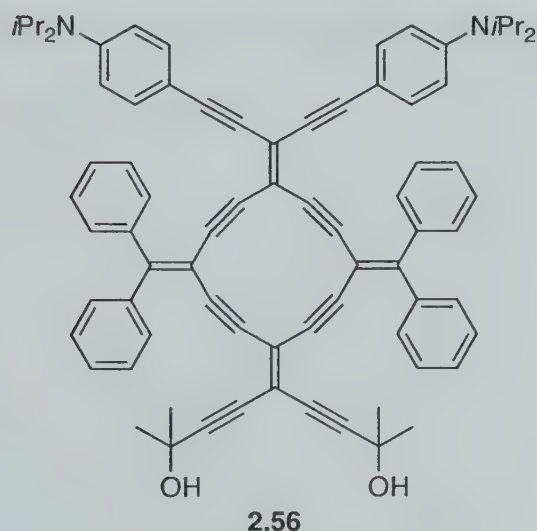
2207, 2169, 1603, 1295 cm^{-1} ; ^1H NMR (500 MHz, CD_2Cl_2) δ 7.47-7.42 (m, 8H), 7.37-7.33 (m, 6H), 7.29 (d, J = 9.1, 4H), 7.27-7.23 (m, 6H), 6.76 (d, J = 9.1 Hz, 4H), 3.90 (septet, J = 6.9 Hz, 4H), 1.29 (d, J = 6.9 Hz, 24H), 0.82 (18H), 0.05 (12H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 158.0, 149.4, 140.9, 140.0, 133.3, 130.8, 130.7, 129.2, 128.8, 128.2, 128.1, 118.8, 115.7, 111.6, 108.9, 103.8, 102.1, 101.7, 96.73, 96.65, 89.8, 87.0, 47.8, 26.2, 21.2, 16.9, -4.7. HRMS MALDI m/z calcd. for $\text{C}_{78}\text{H}_{86}\text{N}_2\text{Si}_2$ (M^+) 1106.6324, found 1106.6325. DSC: Mp = 160 $^\circ\text{C}$.



2.51

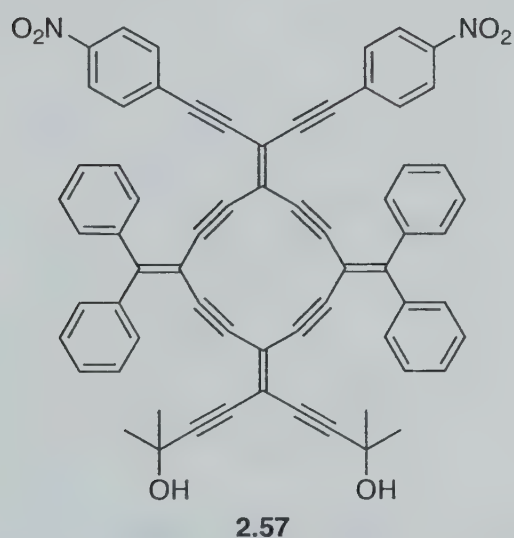
Iso-PDA **2.54** (0.024 g, 0.027 mmol) was desilylated using TBAF (0.05 mL, 0.05 mmol, 1.0 M in THF) and cross-coupled to dibromoolefin **2.22** (0.015g, 0.027 mmol) according to the general procedure F. FCC (silica gel, EtOAc/hexanes 1:9 $\rightarrow$ 3:7) and two-solvent recrystallization using CH_2Cl_2 /hexanes at 5 $^\circ\text{C}$ provided [**4**]ER **2.51** (0.0084 g, 30%) as a yellow solid. Mp 201-202 $^\circ\text{C}$ (discolors, decomp). R_f = 0.52 (EtOAc/hexanes 1:1). UV-vis (CH_2Cl_2) λ_{max} (ϵ) 436 (sh, 29 900), 393 (128 000),

275 (31 000) nm; IR (CH₂Cl₂, cast) 3402 (br), 3083, 3054, 2942, 2865, 2168, 2136, 1278 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.42-7.37 (m, 14H), 7.31-7.28 (m, 6H), 1.45 (s, 2H), 1.31 (s, 12H), 0.94-0.85 (m, 42H); ¹³C NMR (100 MHz, CDCl₃) δ 153.4, 140.6, 139.6, 131.1, 130.8, 129.5, 129.2, 128.0, 127.9, 117.5, 116.8, 111.9, 110.1, 104.0, 103.7, 103.6, 102.7, 102.5, 101.9, 96.2, 95.1, 79.5, 65.4, 30.9, 18.6, 11.2. HRMS MALDI *m/z* calcd. for C₇₂H₇₆O₂Si₂ (M⁺) 1028.5378, found 1028.5377. DSC: Mp 189 °C; decomposition, 203 °C (onset), 205 °C (peak).



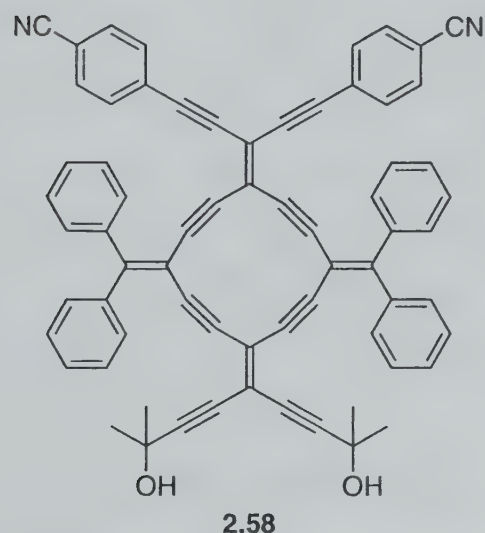
[4]ER 2.51 (0.025 g, 0.024 mmol) was desilylated and cross-coupled to 4-iodo-*N,N*-diisopropylaniline (0.015 g, 0.048 mmol) in the presence of *i*Pr₂NH (2 mL), Pd(PPh₃)₄ (0.001 g, 0.001 mmol), and CuI (0.0004 g, 0.002 mmol) according to general procedure G. FCC (silica gel, EtOAc/hexanes 1:5 → 3:5) followed by washing with Et₂O afforded **[4]ER 2.56** as a red solid (0.019 g, 79%). Mp 233-235 °C (discolors, decomp). *R*_f = 0.38 (EtOAc/hexanes 1:1). UV-vis (CH₂Cl₂) λ_{max} (ε) 544 (25 100), 488 (29 900), 397 (72 600), 387 (73 000), 312 (39 500), 283 (44 100) nm;

IR (CH₂Cl₂, cast) 3375 (br), 3052, 2972, 2928, 2170, 1602, 1294 cm⁻¹; ¹H NMR (500 MHz, CD₂Cl₂) δ 7.49-7.46 (m, 4H), 7.44-7.38 (m, 10H), 7.22-7.18 (m, 4H), 7.16-7.12 (m, 2H), 6.94 (d, *J* = 9.1 Hz, 4H), 6.70 (d, *J* = 9.1 Hz, 4H), 3.92 (septet, *J* = 6.9 Hz, 4H), 1.50 (s, 2H), 1.32 (d, *J* = 6.9 Hz, 24 H), 1.26 (s, 12H); ¹³C NMR (125 MHz, CD₂Cl₂) δ 153.2, 149.3, 140.8, 140.0, 133.2, 131.3, 131.0, 129.7, 129.6, 128.4, 128.3, 117.4, 115.6, 114.2, 112.2, 110.5, 108.6, 104.0, 103.4, 102.7, 102.2, 101.6, 97.3, 95.6, 86.7, 79.5, 65.6, 47.9, 31.1, 21.2. HRMS MALDI *m/z* calcd. for C₇₈H₇₀N₂O₂ (M⁺) 1066.5432, found 1066.5432. DSC: decomposition, 226 °C (onset), 230 °C (peak).



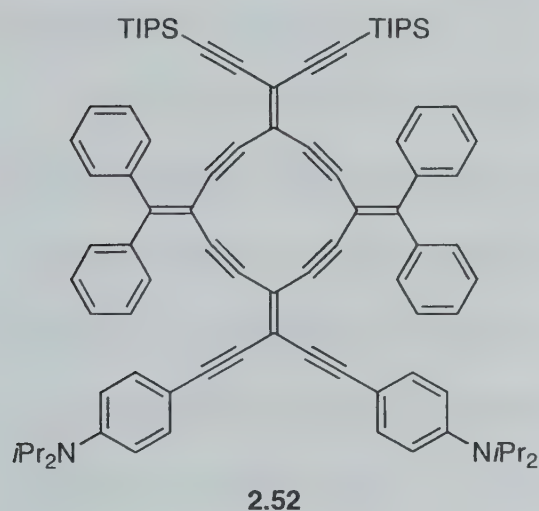
[4]ER 2.51 (0.016 g, 0.016 mmol) was desilylated and cross-coupled to 4-iodonitrobenzene (0.0080 g, 0.032 mmol) in the presence of *i*Pr₂NH (2 mL), Pd(PPh₃)₄ (0.001 g, 0.001 mmol), and CuI (0.0004 g, 0.002 mmol) according to general procedure G. Silica gel filtration (CH₂Cl₂) and washing with Et₂O afforded **[4]ER 2.57** as an orange solid (0.015 g, 99%). Mp 208-210 °C (discolors, decomp). *R*_f = 0.66 (THF/hexanes 1:1).

UV-vis (CH_2Cl_2) λ_{max} (ϵ) 499 (sh, 13 400), 412 (80 300), 277 (34 800) nm; IR (CH_2Cl_2 , cast) 3548, 3446, 3051, 2930, 2170, 1342 cm^{-1} ; ^1H NMR (500 MHz, THF-d_8) δ 8.19 (d, J = 9.0 Hz, 4H), 7.45-7.40 (m, 14H), 7.37 (d, J = 9.0 Hz, 4H), 7.22 (t, J = 8.0 Hz, 4H), 7.04 (t, J = 7.4 Hz, 2H), 4.43 (s, 2H), 1.18 (s, 12H); ^{13}C NMR (125 MHz, THF-d_8) δ 155.8, 148.8, 140.8, 140.5, 133.7, 131.6, 131.5, 130.8, 130.6, 129.3, 129.2, 128.9, 124.3, 121.0, 116.2, 113.3, 109.4, 107.3, 106.2, 103.0, 102.2, 97.0, 96.9, 96.1, 90.9, 79.5, 64.9, 31.7. HRMS MALDI m/z calcd. for $\text{C}_{66}\text{H}_{42}\text{N}_2\text{O}_6$ (M^+) 958.3037, found 958.3035. DSC: decomposition, 179 $^\circ\text{C}$ (onset), 190 $^\circ\text{C}$ (peak).



[4]ER 2.51 (0.025 g, 0.024 mmol) was desilylated and cross-coupled to 4-iodobenzonitrile (0.011 g, 0.048 mmol) in the presence of $i\text{Pr}_2\text{NH}$ (2 mL), $\text{Pd}(\text{PPh}_3)_4$ (0.001 g, 0.001 mmol), and CuI (0.0004 g, 0.002 mmol) according to general procedure G. Silica gel filtration (CH_2Cl_2) followed by washing with Et_2O afforded **[4]ER 2.58** as an orange solid (0.022 g, 99%). R_f = 0.47 (THF/hexanes 1:1). UV-vis (CH_2Cl_2) λ_{max} (ϵ) 494 (sh, 12 200), 408 (91 300), 339 (46 400) nm; IR (CH_2Cl_2 , cast) 3482 (br),

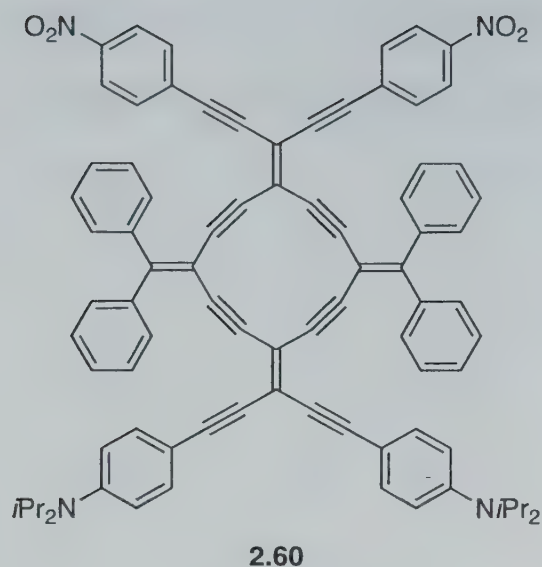
3059, 2981, 2224 1602, 1275 cm^{-1} ; ^1H NMR (500 MHz, THF-d_8) δ 7.69 (d, $J = 8.5$ Hz, 4H), 7.44-7.37 (m, 14H), 7.27 (d, $J = 8.5$ Hz, 4H), 7.22 (t, $J = 7.7$ Hz, 4H), 7.06 (t, $J = 7.4$ Hz, 2H), 4.42 (s, 2H), 1.17 (s, 12H); ^{13}C NMR (125 MHz, THF-d_8) δ 155.6, 140.9, 140.5, 133.3, 132.9, 131.6, 131.4, 130.8, 130.6, 129.3, 128.9, 127.2, 120.5, 118.7, 116.2, 113.7, 113.2, 109.7, 107.0, 106.2, 103.0, 102.2, 97.3, 96.9, 96.1, 90.3, 79.5, 64.9, 31.7. HRMS ESI m/z calcd. for $\text{C}_{68}\text{H}_{42}\text{N}_2\text{O}_2\text{Na}$ ($[\text{M} + \text{Na}]^+$) 941.3139, found 941.3030. DSC: decomposition, 194 $^\circ\text{C}$ (onset), 199 $^\circ\text{C}$ (peak).



Iso-PDA **2.59** (0.310 g, 0.280 mmol) was desilylated using TBAF (0.62 mL, 0.62 mmol, 1.0 M in THF) and cross-coupled with dibromoolefin **2.22** (0.153 g, 0.280 mmol) according to general procedure F. FCC (silica gel, THF/hexanes, 3:10 $\rightarrow$ 3:5) and recrystallization using CH_2Cl_2 /hexanes afforded **[4]ER 2.52** (0.096 g, 27%) as a red solid. Mp 235-237 $^\circ\text{C}$ (discolors, decomp). $R_f =$ (0.34 EtOAc/hexanes 3:17). UV-vis (CH_2Cl_2) λ_{max} (ϵ) 542 (sh, 24 500), 485 (sh, 32 200), 438 (sh, 61 900), 388 (76 400), 292 (48 200) nm; IR (CH_2Cl_2 , cast) 3084, 3053, 2962, 2942, 2865, 2171,

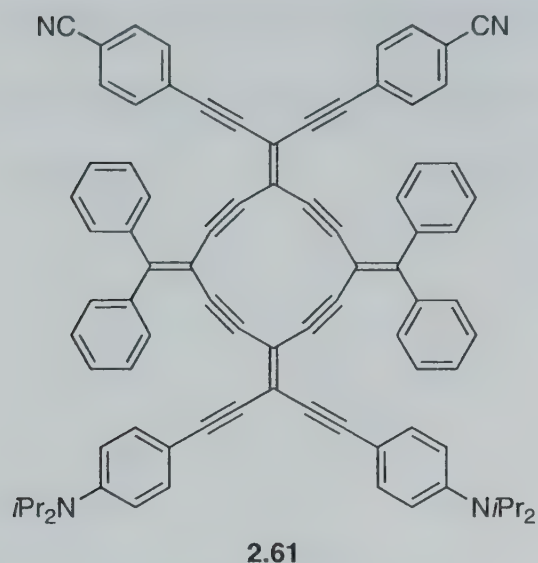
1603, 1295 cm^{-1} ; ^1H NMR (500 MHz, CD_2Cl_2) δ 7.45-7.42 (m, 8H), 7.34-7.31 (m, 6H), 7.17-7.10 (m, 6H), 7.04 (d, $J = 9.1$ Hz, 4H), 6.75 (d, $J = 9.1$ Hz, 4H), 3.93 (septet, $J = 6.9$ Hz, 4H), 1.32 (d, $J = 6.9$ Hz, 24H), 0.95-0.85 (m, 42H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 153.2, 149.3, 140.3, 140.2, 133.1, 131.05, 131.03, 129.7, 129.5, 128.24, 128.20, 117.1, 115.7, 114.0, 112.9, 111.7, 108.8, 104.4, 104.2, 103.14, 103.05, 102.0, 101.2, 96.7, 96.3, 86.6, 47.9, 21.2, 18.8, 11.5. HRMS MALDI m/z calcd. for $\text{C}_{90}\text{H}_{98}\text{N}_2\text{Si}_2$ (M^+) 1262.7263, found 1262.7266. DSC: decomposition, 247 $^\circ\text{C}$ (onset), 289 $^\circ\text{C}$ (peak).

A crystal suitable for X-ray crystallography was grown from a CH_2Cl_2 solution of **2.52** which had been layered with hexanes and allowed to slowly evaporate in the refrigerator at 4 $^\circ\text{C}$. X-ray crystallographic data for **2.52**: $\text{C}_{90}\text{H}_{98}\text{N}_2\text{Si}_2$, $M = 1263.93$; monoclinic space group $P2_1$ (No. 4); $\rho_{\text{calcd}} = 1.085 \text{ g cm}^{-3}$; $a = 13.9906$ (7) $\text{\AA}$, $b = 13.3080$ (6) $\text{\AA}$, $c = 20.9613$ (10) $\text{\AA}$; $\beta = 97.6003$ (7) $^\circ$; $V = 3868.4$ (3) $\text{\AA}^3$; $Z = 2$; $\mu = 0.091 \text{ mm}^{-1}$. Final $R_1(\text{F}) = 0.0362$ (12506 observations) [$F_o^2 \geq 2\sigma(F_o^2)$]; $wR_2 = 0.0841$ for 938 variables, 6 restraints, and 1470 data with [$F_o^2 \geq -3\sigma(F_o^2)$]. Within the disordered triisopropylsilyl group, the Si2A–C33A and Si2B–C33B distances were constrained to be equal (within 0.03 $\text{\AA}$) during refinement. Also within this group, the C33A–C34A, C33A–C35A, C33B–C34B, and C33B–C35B were constrained to be equal within (within 0.05 $\text{\AA}$) during refinement.



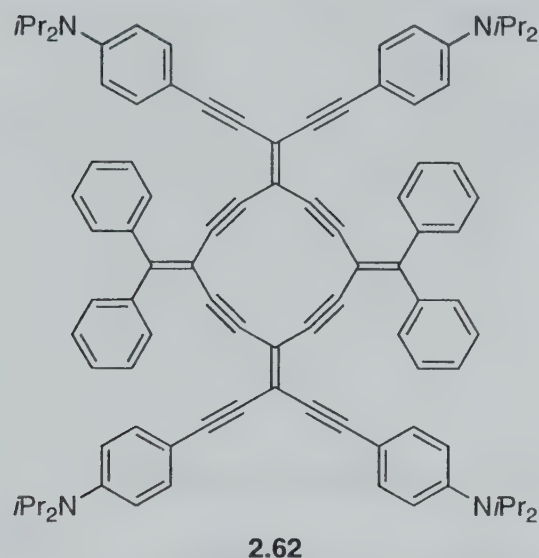
[4]ER 2.52 (0.0258 g, 0.0204 mmol) was desilylated and cross-coupled to 4-iodonitrobenzene (0.0102 g, 0.0408 mmol) in the presence of *i*Pr₂NH (2 mL), Pd(PPh₃)₄ (0.001 g, 0.001 mmol) and CuI (0.0004 g, 0.002 mmol) according to general procedure G. Silica gel filtration (EtOAc/hexanes 3:10) and washing with Et₂O afforded **[4]ER 2.60** as brown solid (0.023 g, 94%). Mp 275-277 °C (discolors, decomp). *R*_f = 0.38 (THF/hexanes 3:7). UV-vis (CH₂Cl₂) λ_{max} (ε) 582 (sh, 9 470), 497 (47 600), 404 (52 600), 295 (45 300); IR (CH₂Cl₂, cast) 3052, 2970, 2169, 1602, 1518 cm⁻¹. ¹H NMR (500 MHz, CD₂Cl₂) δ 8.13 (d, *J* = 9.0 Hz, 4H), 7.52-7.46 (m, 8H), 7.31 (d, *J* = 9.0 Hz, 4H), 7.24-7.15 (m, 10H), 7.01-6.97 (m, 2H), 6.94 (d, *J* = 9.1 Hz, 4H), 6.69 (d, *J* = 9.1 Hz, 4H), 3.93 (septet, *J* = 6.9 Hz, 4H), 1.32 (d, *J* = 6.9 Hz, 24H); ¹³C NMR (125 MHz, CD₂Cl₂) δ 154.2, 149.4, 147.8, 140.3, 139.8, 133.2, 133.1, 131.2, 131.1, 129.9, 129.8, 129.0, 128.4, 128.3, 123.8, 120.7, 115.5, 114.5, 111.9, 108.9, 108.5, 107.0, 102.5, 102.0, 101.8, 97.8, 96.3, 95.9, 91.0, 86.7, 47.9, 21.2. HRMS

MALDI m/z calcd. for $C_{84}H_{64}N_4O_4$ (M^+) 1192.4922, found 1192.4919. DSC: decomposition, 260 °C (onset), 270 °C (peak).



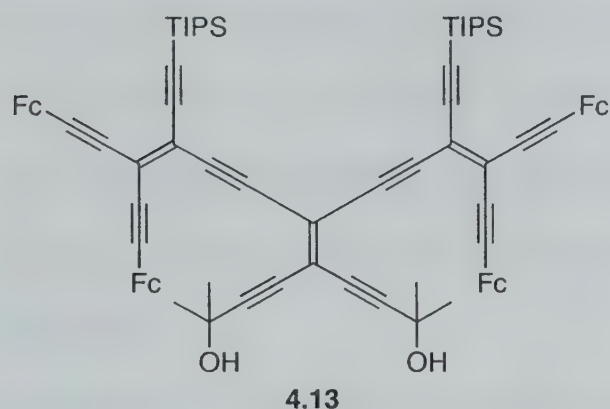
[4]ER 2.52 (0.026 g, 0.021 mmol) was desilylated and coupled to 4-iodobenzonitrile (0.010 g, 0.042 mmol) in the presence of iPr_2NH (2 mL), $Pd(PPh_3)_4$ (0.001 g, 0.001 mmol), and CuI (0.0004 g, 0.002 mmol) according to general procedure G. FCC (silica gel, EtOAc/hexanes 1:10 → 3:10) afforded **[4]ER 2.61** as a brown solid (0.0099 g, 41%). Mp 253-255 °C (discolors, decomp). R_f = 0.48 (EtOAc/hexanes 3:7). UV-vis (CH_2Cl_2) λ_{max} (ϵ) 573 (sh, 15 200), 485 (65 200), 403 (70 600), 317 (61 100); IR (CH_2Cl_2 , cast) 3054, 2969, 2919, 2227, 2170, 1602, 1294 cm^{-1} ; 1H NMR (500 MHz, CD_2Cl_2) δ 7.57 (d, J = 8.6 Hz, 4H), 7.51-7.49 (m, 4H), 7.47-7.45 (m, 4H), 7.24-7.20 (m, 8H), 7.19-7.14 (m, 6H), 7.00-6.96 (m, 2H), 6.94 (d, J = 9.1 Hz, 4H), 6.69 (d, J = 9.1 Hz, 4H), 3.92 (septet, J = 6.9 Hz, 4H), 1.32 (d, J = 6.9 Hz, 24H); ^{13}C -NMR (125 MHz, CD_2Cl_2) δ 154.0, 149.3, 140.3, 139.8, 133.2, 132.7, 132.3, 131.14, 131.08, 129.9, 129.7, 128.4,

128.2, 127.0, 120.2, 118.7, 115.5, 114.5, 112.6, 112.0, 109.2, 108.5, 106.6, 102.5, 102.0, 101.8, 97.8, 96.6, 95.9, 90.2, 86.7, 47.8, 21.2. HRMS MALDI m/z calcd. for $C_{86}H_{64}N_4$ (M^+) 1152.5126, found 1152.5123. DSC: decomposition, 244 °C (onset), 251 °C (peak).



[4]ER 2.52 (0.025 g, 0.020 mmol) was desilylated and cross-coupled to 4-iodo-*N,N*-diisopropylaniline (0.015 g, 0.040 mmol) in the presence of iPr_2NH (2 mL), $Pd(PPh_3)_4$ (0.001 g, 0.001 mmol), and CuI (0.0004 g, 0.002 mmol) according to general procedure G. Silica gel filtration (MeOH/ CH_2Cl_2 3:100) and washing with Et_2O afforded **[4]ER 2.62** as a red solid (0.010 g, 40%). Mp 287 °C (discolors, decomp). R_f = 0.31 (THF/hexanes 3:7). UV-vis (CH_2Cl_2) λ_{max} (ϵ) 545 (sh, 59 400), 492 (75 000), 408 (80 500), 293 (72 000); IR (CH_2Cl_2 , cast) 2954, 2925, 2171 cm^{-1} ; 1H NMR (500 MHz, CD_2Cl_2) δ 7.50-7.49 (dd, J = 8.5 Hz, J = 8.3 Hz, 8H), 7.23-7.19 (m, 8H), 7.14-7.10 (tt, J = 7.4 Hz, J = 1.5 Hz, 4H), 6.94 (d, J = 9.1 Hz, 8H), 6.70 (d, J = 9.1 Hz, 8H), 3.92 (septet, J = 6.8 Hz, 8H), 1.32 (d, J = 6.8 Hz, 48H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 152.0, 149.3,

140.4, 133.2, 131.1, 129.4, 128.3, 115.6, 113.8, 112.7, 108.8, 103.2, 102.5, 101.3, 97.4, 86.7, 47.8, 21.2. HRMS MALDI m/z calcd. for $C_{96}H_{92}N_4$ (M^+) 1300.7317, found 1300.7312. DSC: decomposition, 271 °C (onset), 303 °C (peak).



TEE **2.27** (0.06060 g, 0.1097 mmol) was desilylated using TBAF (1.2 mL, 1.2 mmol, 1.0 M in THF) and cross-coupled to ferrocenyl vinyl triflate³ (0.2001 g, 0.2742 mmol) in deoxygenated THF (5 mL) in the presence of $Pd(PPh_3)_4$ (0.006 g, 0.005 mmol), iPr_2NH (2mL) and, CuI (0.0021 g, 0.011 mmol) for 36 h at reflux according to general procedure E. FCC (silica gel, EtOAc/hexanes 1:5 $\rightarrow$ 1:1) provided compound **4.13** (0.0489 g, 30%) as a dark-red foam. Mp . R_f = 0.41 (EtOAc/hexanes 3:7). IR (CH_2Cl_2 , microscope) 3404 (br), 3082, 3097, 2943, 2954, 2865, 2184, 2142, 1463, 1250 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$) δ 4.60 (t, J = 1.9 Hz, 4H), 4.50 (t, J = 1.9 Hz, 4H), 4.30-4.29 (m, 8H), 4.24 (s, 8H), 4.23 (s, 8H), 2.03 (s, 2H), 1.56 (s, 12H), 1.14 (s, 42H); ^{13}C NMR (125 MHz, $CDCl_3$, APT) δ 121.5, 118.0, 112.0, 104.3, 103.5, 101.2, 101.0, 100.5, 96.8, 93.7, 85.0, 84.7, 80.0, 72.3, 71.9, 70.5, 70.2, 69.8, 69.7, 65.7, 64.0, 63.8, 31.2, 18.9, 11.4 (one signal coincident or not observed). HRMS MALDI m/z

calcd. for $\text{C}_{90}\text{H}_{92}\text{Fe}_4\text{O}_2\text{Si}_2$ (M)⁺ 1484.4028, found 1484.4029. DSC: decomposition, 137 °C (onset), 174 °C (peak).

References and notes

(1) Zhao, Y. M.; Slepko, A. D.; Akoto, C. O.; McDonald, R.; Hegmann, F. A.; Tykwinski, R. R. *Chem. Eur. J.* **2005**, *11*, 321-329.

(2) The bisdeprotected **2.53** was carried on to the subsequent step without further purification and yields are calculated based on the bisdeprotected *iso*-PDA.

(3) Rankin, T.; Tykwinski, R. R. *Org. Lett.* **2003**, *5*, 213-216.

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